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W. A. EVERHART

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THE HISTORY OF KEYS AND PHYLOGENETIC TREES IN SYSTEMATIC BIOLOGY[1]

EDWARD G. VOSS[2]

I. THE ANCIENT ROOTS

The germs of many biological ideas which were clearly developed at a much later date can be sought among the ancient Greeks. It is so with our topic of the development of analytical keys and phylogenetic trees, for it is with Aristotle that we find the rudimentary notions of thinking in the lines which these more modern mechanical devices represent.

It is true that even the Sumerians of 3000 B.C. had made lists of birds, fishes, domestic animals, plants, and implements, but these first steps in a scientific classification can scarcely be compared with the systematization of Aristotle. Undoubtedly influenced by his great teacher, Plato, Aristotle became "the greatest collector and systematizer of knowledge whom the ancient world produced." (Dampier, p. 29.) Observing that "animals differ from one another in their modes of subsistence, in their actions, in their habits, and in their parts" (Book I, ch. 1), he proceeded with some attempts at classification, with the help of as many characteristics as possible. Typical of his method of classification are the following passages:

> Of land animals some are furnished with wings, such as birds and bees, and these are so furnished in different ways one from another; others are furnished with feet. Of the animals that are furnished with feet some walk, some creep, and some wriggle. (Book I, ch. 1.)
>
> Of creatures that can fly and are bloodless some are coleopterous or sheath-winged . . .; others are sheathless, and of these latter some are dipterous and some tetrapterous. (Book I, ch. 5.)

These paragraphs differ from keys in at least two fundamental ways: the mechanical form and the omission of names to which the analysis of a key would lead one. Imagine them, however, set up this way:

Land Animals
  With wings
    Bloodless
      Coleopterous ..... _____
      Not coleopterous
        Dipterous ..... _____
        Tetrapterous ..... _____

---

[1] Paper from the Department of Botany and the Botanical Gardens of the University of Michigan, No. 958. Submitted in December 1951.

[2] Class of 1950, Denison University.

Not bloodless
With feet
Walking animals ..... _____
Creeping animals ..... _____
Wriggling animals ..... _____
Not land animals

The ultimate groups are not unified categories according to modern taxonomic conceptions, but the organization exemplified by a key is there.

Aristotle's pupil and successor, Theophrastus, had a similar classificatory instinct, but applied it to botany. Theophrastus tended more toward the sort of dichotomy that Aristotle had avoided—placing all organisms in two categories on the basis of a particular characteristic, then dividing them all over again on the basis of another characteristic. In such observations as the following, however, he refers to subdivisions:

> . . . some leaves have no leaf-stalk, as those of squill and purse-tassels, while others have a leaf-stalk. And some of the latter have a long leaf-stalk, as vine and ivy, some, as olive, a short one. (Book I, ch. x:7.)
>
> Again of herbaceous plants too some have several stems, some only one; and of the latter some have no side-shoots along the stem, while others have side-shoots. . . . Those with prostrate stems have generally more than one, while those with erect stems have but one or a few. Of these those with smooth stems have no side-shoots, as onion, leek, garlic —the wild, as well as the cultivated forms; and of these again some have straight, some crooked stems. (Book VII, ch. viii:2.)

As evidence that the idea of dichotomy leading to subordinate categories of arrangement was not limited to the Western world, we can cite the Chinese herbalist Pao Shan, who wrote the rare famine herbal, the *Yeh-ts'ai po-lu*, following an arrangement that probably was centuries older than his own time (17th cent.):

> Now, I have collected together these wild vegetables . . . dividing them so as to make a *ts'ao-pu* or herbaceous plant section in 2 *chüan* and a *mu-pu* or tree section in 1 *chüan*. These materials are arranged according to their nature and taste, with explanations telling how to season and prepare them, and I have drawn pictures to illustrate them; thus, after an examination of this book, venerable men of the wildernesses and children of the mountains will know how to gather edible wild plants . . . (Swingle, p. 188.)

Here was a systematic arrangement specifically designed for aid in the identification of plants.

These ancient arrangements of the Greeks and the Chinese have been mentioned simply to demonstrate the deep and apparently natural roots of the idea that organisms are more easily distinguished when grouped under contrasting categories arranged in a hierarchic order. Before taking up the question of keys again with the outlines of the 17th century European writers, let us look into the vague origins of the idea of phylogeny and its mechanical expression.

Several philosophers, including Anaximander and Empedocles, had hinted at ideas of "evolution" but in this approach again Aristotle was the outstanding

Greek thinker. It would be stretching a point to consider him a direct forerunner of Darwin, but it cannot be denied that Aristotle's works suggest a simple phylogenetic series, somewhat like the order of creation in older cosmogonies.

> Nature proceeds little by little from things lifeless to animal life in such a way that it is impossible to determine the exact line of demarcation, nor on which side thereof an intermediate form should lie. (Book VIII, ch. 1.)

To his credit in the field of evolution may be stated Aristotle's belief in natural law as the source of evolutionary change and his belief in the development of modern organisms from a primordial mass. (Cf. Lindsey, p. 7.) Aristotle added to the earlier opinions that the development of life is a gradual process the conception that the more perfect type might not only have followed in time but also have actually developed out of the less perfect. (Cf. Dampier, p. 273.) Aristotle's "ladder of life" idea remained with the field of philosophy, and it was several centuries before a biologist seriously expanded the concept.

II. THE DEVELOPMENT OF KEYS

In the works of the 17th century naturalists, such as Morison, Ray, and Rivinus, we find diagrams which might be considered the first analytical keys. Several systems of classification had preceded these men, who were led, however, to organize their systems in an outline form which is in effect an early type of key. Figure 1 reproduces such a "key" from the first volume of Ray's *Historia Plantarum* (1686), and figure 2, one from the last edition of the *Methodus Plantarum* (1703). A similar treatment in the animal kingdom is shown in figure 3, which is the only such "key" in the *Historia Piscium* (1686). In figure 4 is given an arrangement published in 1699 by Rivinus (who rendered thus in Latin his real name, Bachmann) in his *Introductio Generalis in Rem Herbariam.* In the work which passes as the first part of his "Historia Plantarum," the *Plantarum Umbelliferarum Distributio Nova* (1672), Morison introduced very similar bracketed outlines, a feature continued in later parts.

Although he himself prepared no keys to plants, to the English anatomist Nehemiah Grew belongs the credit for first clearly describing the idea. The second part of book four of Grew's *Anatomy of Plants* (1682) is on the anatomy of flowers, and was read before the Royal Society on November 9, 1676. An appendix to this part is headed as "*Being a* Method *proposed, for the ready finding, by the* Leaf *and* Flower, *to what Sort any* Plant *belongeth.*" (p. 174–176.) He introduces his subject as follows:

> Although many have bestowed extraordinary Care and Industry upon the searching out, and Description of *Plants*; and for the reducing of them to their several *Tribes*: yet I will take leave, here to propose a short *Method* whereby Learners, seeing a *Plant* they know not, may be informed to what Sort it belongs, and so be directed where to find it described and discoursed of. For, except they have a Master to conduct them, which few have; they must needs, by seeking at random, lose a great deal of time, which by a regular Enquiry might be saved.

He then suggests that flowers and leaves would be the most satisfactory in distinguishing plants for such a purpose, as they are "the most *Conspicuous*, and in those *Parts*, where the Learner may the most readily and without any difficulty take notice of them . . ." There follow eighteen suggestions of charac-

Herbarum Aſperifoliarum TABULA.

Herbæ aſperifoliæ, quibus folia in caulibus alterna, flores monopetali marginibus quinquepartitis, inciſuris alias profundioribus alias levioribus, ſingulis autem floribus quatuor plerumque ſuccedunt ſemina, ſunt vel ſeminibus ad ſingulos flores

- *Quaternis*, perianthio
  - *Oblongo integro*, foliis maculis albis variis; PULMONARIA MACULOSA.
  - *Breviore* & ad modum floris expanſo; ſeminibus
    - *Aſperis* & lappaceis, foliis in pleriſque ſpeciebus mollibus & graviter odoratis; CYNOGLOSSA.
    - *Rugoſis*,
      - *Caput viperinum aut galeam referentibus*, flore
        - *In quinque lacinias* totidem folia imitantes *diviſo*, radicibus
          - *Albis*, florum laciniis
            - *Obtuſis* & ſubrotundis, foliis longis acutis; BUGLOSSA.
            - *Acutis*, foliis brevibus & latioribus; BORAGO.
          - *Rubris*; ANCHUSA.
        - *Corniculato*; parte ſuperiore longiùs excurrente, inferiore breviore; ECHIUM.
      - *Scyphum referentibus*, foliis lævibus Lini, floro lacteo; LINUM UMBILICATUM.
    - *Lævibus*,
      - *Non ſplendentibus*, floribus
        - *In ſpicas longas recurvas*, foliis lanuginoſis; HELIOTROPIUM *majus*.
        - *Ad foliorum alas*, caulibus aſperis & veſtibus adhærentibus, ſeminibus compreſſis; APARINE *major*.
      - *Splendentibus* & velut politis floribus
        - *Cylindraceis tubuloſis*, foliis amplis longis; CONSOLIDA *major*.
        - *In quinque lacinias expanſis*;
          - *Major*, ſeminibus duris ſplendentibus; LITHOSPERMUM.
          - *Minor*, echioides, ſpicis florum prælongis recurvis, *Echium* SCORPIOIDES.
- *Binis*, flore cylindraceo tubuloſo, folio glauco; CERINTHE.

FIGURE 1. Ray's "Table of Rough-leaved Plants" from the *Historia Plantarum* (1686, Vol. I, p. 488), reduced to approximately five-eighths original size.

teristics to look for in leaves and flowers: size, shape, texture, arrangement, margin, color, etc. In conclusion, Grew states:

> How far these, and some other like *Distinctions*, being reduced to *Tables*, would serve for the finding out of any Sort of *Plant*, may be conceived, if we consider, how great a Variety, a few *Bells*, in the ringing of Changes, will produce. And the search will be easy, and successful, if in every foregoing *Table*, reference be made to those that follow; and in the *Tables* conteining the last *Divisions*, the Names of the *Plants* therein poynted out, be expressed.

In some miscellaneous lectures at the end of his *Anatomy*, Grew presents a "Tabula, quae Genericas omnes Saporum differentias comprehendit" (Lecture VI, table on p. 295). This table does not involve taxa, but only types of "savors"; it is far from being dichotomous (indeed, he never suggested dichotomy as a virtue in his proposed "method"); and it often leads clearly to *examples* of types rather than distinguishing between every kind. It is set up in a bracketed form very similar to that of Ray and Rivinus, but clearly is not designed for identification.

Herbæ enangioſpermæ ſeu vaſculiferæ flore monopetalo ſunt vel eodem.

Uniformi ſeu regulari, variorum generum,
- *Integro*, vel in lacinias minus profundas ſecto; ut CONVOLVULUS, NICOTIANA &c.
- *Tetrapetalum referente* ſeu tetrapetaloide; ut VERONICA &c.
- *Pentapetalum referente*; ſeu pentapetaloide
  - *Unicapſulares*; quibus ſeminum ſedes in medio eſt, exterius protegente vaſculo; ANAGALLIS. &c.
  - *Bicapſulares*; ſeu vaſculo in duo loculamenta diviſo ut CENTAURIUM MINUS. &c.
  - *Multicapſulares*, ſeu vaſculo in multa, id eſt plura duobus, loculamenta ſeu thecas diviſo; VALERIANA GRÆCA. &c.

Diſformi ſeu irregulari,
- *Figura varia*; ARISTOLOCHIA &c.
- *Galeato aut labiato*; MELAMPYRUM &c.
- *Rictum exprimente*
  - *Calcari prædito*; LINARIA.
  - *Calcari carente*; ANTIRRHINUM &c.

FIGURE 2. An example from Ray's *Methodus* of 1703 (p. 80), reproduced natural size

Morison, followed closely by Ray and Rivinus, appears to have been the first to use these bracketed tables to any extent in classifying organisms in a purely biological work, but where did the idea originate? It is clear that the method was developed before the proposal of Grew, as Morison's first tables were published four years before Grew's paper was read. Ray, however, had written such tables in 1666 for Wilkins' *Real Character*, which was published two years later. Wilkins' work was an attempt to simplify English speech and put it on a universal foundation. Bracketed tables were extensively employed, especially in the second part "Conteining a regular enumeration and description of all those things and notions to which names are to be assigned." (p. 22–296.) The book reminds one of a small encyclopedia and Roget's Thesaurus rolled into one and outlined in bracketed form. In explaining his tables, Wilkins says

These *Species* are commonly joyned together by *pairs*, for the better helping of the Memory, (and so likewise are some of the *Genus*'s and *Differences*.) Those things which naturally have *Opposites*, are joyned with them, according to such Opposition, whether

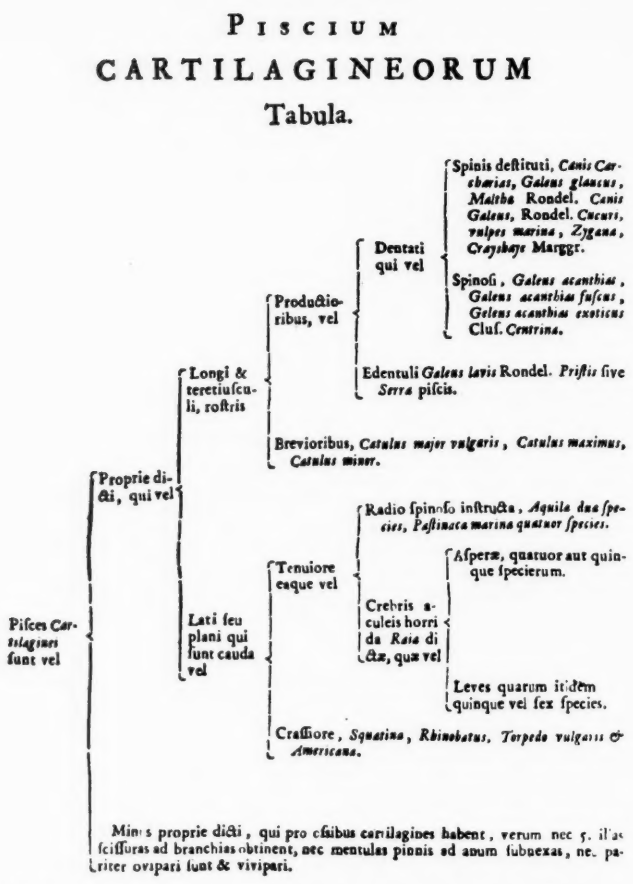
PISCIUM
CARTILAGINEORUM
Tabula.
Pisces Cartilaginei sunt vel
Proprie dicti, qui vel
Longi & teretiusculi, rostris
Productioribus, vel
Dentati qui vel
Spinis destituti, Canis Carcharias, Galeus glaucus, Maltha Rondel. Canis Galeus, Rondel. Cucuri, vulpes marina, Zygæna, Crayshoye Marggr.
Spinosi, Galeus acanthias, Galeus acanthias fuscus, Galeus acanthias exoticus Cluf. Centrina.
Edentuli Galeus lævis Rondel. Priftis five Serra pifcis.
Brevioribus, Catulus major vulgaris, Catulus maximus, Catulus minor.
Lati seu plani qui sunt cauda vel
Tenuiore eaque vel
Radio spinoso instructa, Aquila duæ fpecies, Paftinaca marina quatuor fpecies.
Crebris aculeis horrida Raia di ctæ, quæ vel
Asperæ, quatuor aut quinque fpecierum.
Leves quarum itidem quinque vel fex fpecies.
Craffiore, Squatina, Rhinobatus, Torpedo vulgaris & Americana.
Minus proprie dicti, qui pro cæibus cartilagines habent, verum nec 5. illas fciffuras ad branchias obtinent, nec mentulas pinnis ad anum fubnexas, neque pariter ovipari funt & vivipari.

FIGURE 3. Ray's table of the cartilaginous fish, from the *Historia Piscium* (1686, p. 46), reduced to slightly over one-half original size. Although Ray ostensibly published this volume as a posthumous work of Francis Willughby, there is considerable evidence that most of the work is Ray's own. (Cf. Raven, p. 339–370.)

Single or *Double*. Those things that have no Opposites, are paired together with respect to some *Affinity* which they have one to another. (p. 22.)

He considers in this fashion a great variety of subjects, including action, discourse, plants, animals, space, operation, judicial and military matters, etc. The plant and animal tables were contributed by John Ray and Francis Willughby, respectively, but the idea of such tables is Wilkins' own. Ray himself did not care for having to fit his supposedly natural classification to so artificial and mystical a system as Wilkins imposed upon him, and we can scarcely believe that he had so clear an idea of the practicality of an artificial analysis for the *purpose of identification* as Grew obviously had.

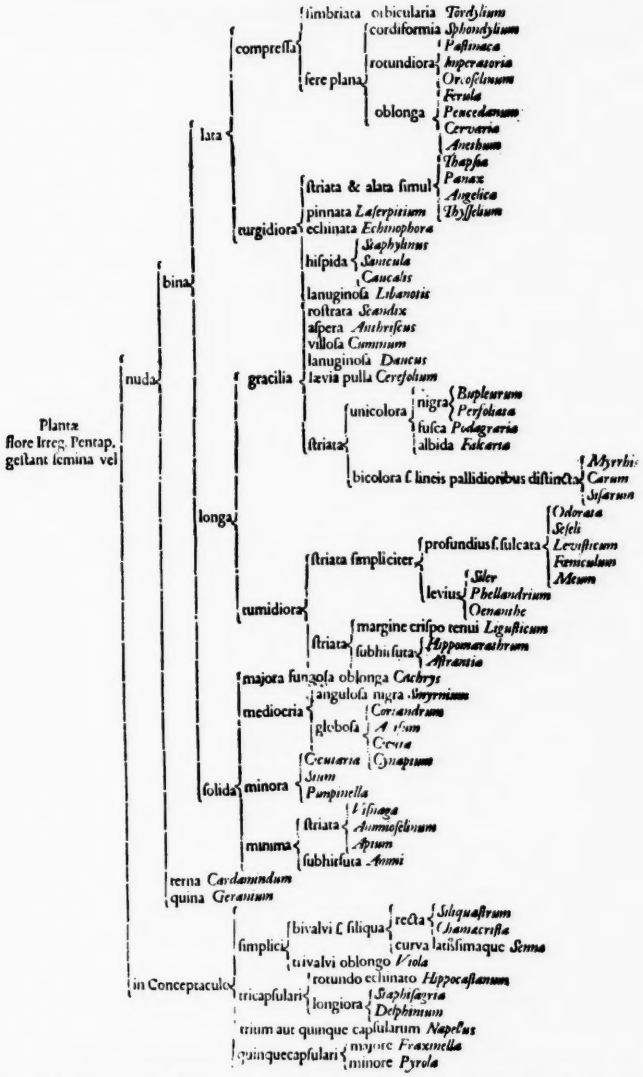

FIGURE 4. A table from Rivinus' *Introductio Generalis in Rem Herbariam* (p. 11 of the last part (1699) in which he treats the "order of plants having an irregular pentapetalous flower"), reduced approximately one-half. Note that in this "key," as in those of Ray, each word or phrase in the table is grammatically a fragment of a full sentence which in its completeness describes the plant in question.

Bracketed outlines had been used prior to this time, and there is the possibility that both Ray and Wilkins, as well as Grew, had been at least in part

influenced by the way in which Prince Fredericus Caesius had set up his Phytosophicae Tabulae, appended to Recchus' version of Hernández' *Thesaurus Rerum Medicarum* as edited for the Academy of the Lynx. A portion of one of the tables of Caesius is reproduced in figure 5 as an example of what appears to have been the first published arrangement of biological knowledge in just this way. These tables of Caesius were not keys to organisms, but summaries of botanical science in outline form. Their possible influence on the mechanical way in which Ray summarized his classification is not known, although in the preface to the *Historia Plantarum* Ray does indicate that he was familiar with the work of Hernández. It was 1651 before Hernández' volume was published, although it was ready for publication in 1628, after a considerable amount of material had been added to what Recchus had extracted from the original of Hernández (who died in 1587). (Cf. Bartlett, 1949, p. 30–32, & Standley, p. 10–13.)

Whatever the origins of their tabular method may have been, Ray and his contemporaries at least took a great step toward our modern idea of keys. The bracketed outlines of these naturalists do not quite qualify in intent, or always in mechanics, as true keys: they do not always lead to a single name (note especially Rivinus, and Ray's *Methodus*, in which it is clear that the "key" is really a synopsis of a classification, not an analysis for the purpose of identifying specimens); and they are often far from being dichotomous. They are, in general, more analogous to the "synoptic keys" of the earlier editions of Gray's *Manual* (*e.g.*, to Cruciferae, Labiatae, and Compositae in the 7th ed.) and many other British and American works of the 19th and early 20th centuries than they are to "artificial keys."[3]

In the Preface to his *Familles des Plantes* (1763), Adanson outlined the classifications proposed for plants from Theophrastus to Allioni (1762). It is surprising that these various "natural" classifications, especially those of the late 17th and early and middle 18th centuries did not lead to the development of dichotomous keys clearly designed for the *identification* of plants. Instead, the first keys of a really modern type were admittedly artificial. These were Lamarck's strictly dichotomous keys to the plants (including cryptogams) of France in his first book, the *Flore Française* of 1778. Bather (p. lxvi–lxvii) has pointed out the true nature of a key and its first introduction into biology:

> A Key is not a classification, but a method of analysis. The idea was first explicitly brought forward by Lamarck at the very beginning of his career. Having asserted that every species of French plant could be more readily determined by a purely arbitrary analytic key than by the Linnean system with its mixture of supposed reality and ordered arbitrariness he was challenged to produce such a key, and this he did within twelve months. . . .

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[3] "*Keys* are devices useful in identifying an unknown. . . . A key is an artificial analytical device or arrangement whereby a choice is provided between two contradictory propositions. . . . A *synopsis* is a device, usually in the format of a key, presenting graphically the technical characters which in general or in the aggregate differentiate taxa. It is not designed ordinarily for use in identification."

—Lawrence, p. 225.

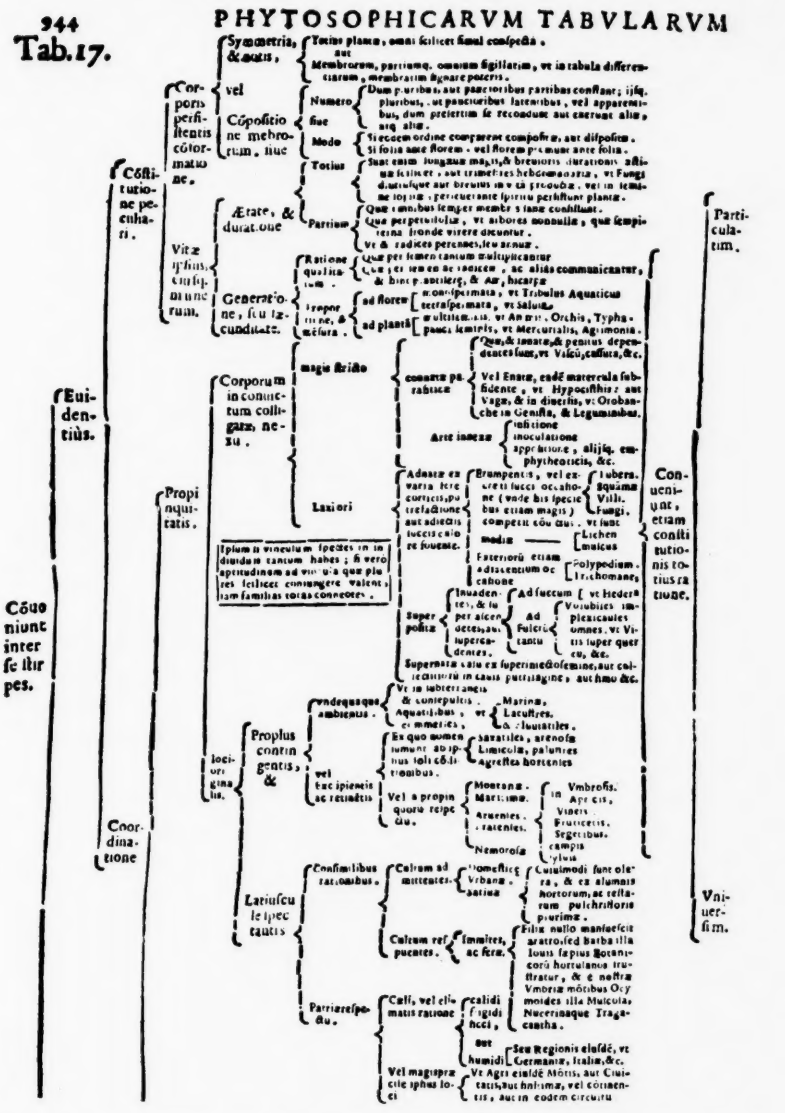

FIGURE 5. Part of a table from the *Phytosophicarum Tabularum . . . Prima Pars* which Prince Fredericus Caesius appended on pages 901–952 of the edition of Hernández' *Thesaurus Rerum Medicarum* published by the Academy of the Lynx in 1651. Reduced to approximately two-thirds original size; portions from extreme right and bottom not shown.

After some years of botanical work, Lamarck's main attention turned to zoology, and the third edition of the *Flore Française* was prepared by his friend

A. P. de Candolle. The "Discours Préliminaire" of the first edition was reprinted on pages 1–60 of the third edition; pages 29–43 present in some detail the philosophy of key-building in an essay fully illustrated with examples of how the new artificial method works and on what principles it is based.[4] De Candolle's letter of dedication to Lamarck (p. v–xvi) gives such good advice concerning the use of keys that it is appropriate to quote it rather fully (p. viii–ix):

> As to the artificial method, I have, without hesitation, given preference to the one which you have contrived, and which consists of leading the student to the name of the plant by always forcing him to choose between two contradictory characters: in this analytic method I have permitted myself only the slight changes necessitated by the increase in the number of plants described. There, after your example, I have sought to distinguish the plants by the easiest and most apparent characters; and when these characters were not constant, I have tried to foresee their aberrations and to arrive at the same name by different routes; but this ease in the distinguishing of plants is very different in different families: in some, such as the crucifers, it is impossible to distinguish the genera without examination of the fruit. . . . When beginners undergo these difficulties in the use of the analytic method, I beg them, before blaming it, to reflect that the most accomplished botanists meet with the same embarrassment, and that no method can make the work easier to students than it is to the masters. . . . But when the pupil knows the name, let him take care not to think he knows the thing! Referred by a number in the analytic method to the description, he will find in this second part the details which put together constitute the whole science.[5]

These words of explanation and advice have scarcely been improved upon from the time of the 3rd edition of the first key to the present time! Following Lamarck's keys to genera are the keys to species; reproduced as a typical example is the first of these, the key to the species of *Nostoc*, in figure 6.

Since Lamarck's key, there have been very few fundamental innovations in the mechanics of key-making. His type, in which the two contrasting leads (forming a *couplet*) are together, has been called the bracketed or *parallel* type, and in modern literature seems to be of more widespread use among zoologists than among botanists.[6] The latter, for the most part, have preferred an *in-*

[4] For some very thorough suggestions for the writing of keys today, see Lawrence, p. 225–228, and also Harrington.

[5] *Quant à la méthode artificielle, j'ai, sans hésiter, donné la préférence à celle que vous avez imaginée, et qui consiste à conduire l'élève au nom de la plante, en le forçant toujours à choisir entre deux caractères contradictoires: dans cette méthode analytique, je ne me suis permis que les légers changemens nécessités par l'augmentation du nombre des plantes décrites. Là, d'après votre example, j'ai cherché à faire distinguer les plantes d'après les caractères les plus faciles et les plus apparens; et lorsque ces caractères n'étoient pas constans, j'ai tenté de prévoir leurs aberrations et de faire arriver au même nom par différentes routes; mais cette facilité dans la distinction des plantes, est très-différente dans différentes familles: dans quelques-unes, telles que les crucifères, il est impossible de distinguer les genres sans l'examen des fruits; . . . lorsque les commençans éprouveront ces difficultés dans l'emploi de la méthode analytique, je les prie, avant de la blâmer, de réfléchir que les Botanistes les plus consommés éprouvent le même embarras, et qu'aucune méthode ne peut rendre le travail plus facile aux élèves, qu'il ne l'est aux maîtres. . . . Mais lorsque l'élève saura le nom, qu'il se garde de croire savoir la chose! Renvoyé par un numéro de la méthode analytique à la description, il trouvera dans cette seconde partie les détails dont l'ensemble constitue la science.*

[6] Some botanists have been known to refer slightingly to these as "entomological keys."

ANALYSE DES ESPÈCES.

I. NOSTOCH. *NOSTOCH.*

1. { Plantes aquatiques..... *N. à verrues* (7).
   { Plantes non aquatiques..... 2.
2. { Plante lobée ou plissée..... 3.
   { Plante arrondie et non lobée ni plissée..... ..... 6.
3. { Peau ou enveloppe membraneuse..... 4.
   { Peau cartilagineuse..... 5.
4. { Plante verdâtre croissant sur la terre... *N. commun* (1).
   { Plante d'un verd noirâtre croissant sur les pierres ou les écorces..... ..... *N. lichenoïde* (3).
5. { Plante d'un brun jaunâtre..... *N. coriace* (2).
   { Plante d'un verd bleuâtre..... *N. découpé* (5).
6. { Plante fixée au sol par une radicule latérale..... ..... *N. en vessie* (4).
   { Point de racines ni de crampons..... 7.
7. { Globules sphériques souvent agglomérés..... ..... *N. sphérique* (6).
   { Globules irréguliers ordinairement distincts..... ..... *N. commun* (1).

FIGURE 6. Lamarck's key to *Nostoc* from his *Flore Française* (3rd ed. by de Candolle, 1815, p. 76), reproduced natural size. Note that *N. commun* is keyed down twice, in accordance with de Candolle's explanation that the same name had sometimes been arrived at by different routes.

dented type, in which all subsequent choices to which a given lead in the key directs the user are arranged under that choice. Lamarck's key reproduced in figure 6 would appear as follows if set in the indented form:

1. Plantes aquatiques ..... *N. à verrues*
1. Plantes non aquatiques
  2. Plante lobée ou plissée
    3. Peau ou enveloppe membraneuse
      4. Plante verdâtre croissant sur la terre ..... *N. commun*
      4. Plante d'un verd noirâtre croissant sur les pierres ou les écorces ..... *N. lichenoïde*
    3. Peau cartilagineuse
      5. Plante d'un brun jaunâtre ..... *N. coriace*
      5. Plante d'un verd bleuâtre ..... *N. découpé*
  2. Plante arrondie et non lobée ni plissée
    6. Plante fixée au sol par une radicule latérale ..... *N. en vessie*
    6. Point de racines ni de crampons
      7. Globules sphériques souvent agglomérés ..... *N. sphérique*
      7. Globules irréguliers ordinairement distincts ..... *N. commun*

The parallel type lends itself somewhat better to long keys in which a large number of species (or other taxa) are included in one key. Among the many current examples which could be cited are Edwards' *Beetles East of the Great*

Plains (which has 291 couplets in one key), Eddy and Hodson's *Taxonomic Keys*, Fassett's *Manual of Aquatic Plants*, Smith's *North American Species of Mycena*, and Smith's *Fresh-water Algae of the United States* (which has a generic key of 537 couplets!). Some brief suggestions for uniformity in the preparation of a key of this type have been given by Williamson.

The indented type of key, although less economical of space, gives a better picture of all that has been involved in reaching a given point in the key, thus making it easier to "work the key backwards." This type is exemplified in Comstock's *Introduction to Entomology*, Blanchard's *Revision of the King Snakes*, Victorin's *Flore Laurentienne*, and Deam's *Flora of Indiana*. The indented form, as skillfully used by Fernald in the 8th edition of Gray's *Manual*, is well-adapted to arranging the species in their "natural order" as they key down. Both types of key are employed in Tryon's *Ferns of Wisconsin* and in the first part of Forbes' *Lepidoptera of New York*. In these two volumes, the parallel form is used for long opening keys (species, based on sterile fronds, and families, respectively) and the indented form for the shorter keys throughout the text.

Alphonso Wood was apparently the first American to employ keys (cf. Merrill, p. 113). In the first (1845) edition of his *Class-Book*, he prefaces Part Second with this excellent explanation (p. 1):

> The following *analytical tables*, founded upon the artificial arrangement of Linnaeus, together with those of the suceeding pages under each natural order, are designed and presented simply as a mode of botanic analysis, which is, in some respects, *new* and *improved*. They are the result of much labor and investigation, since each character employed, required a previous examination of all the species included under it. They reduce the process of analysis to a simple series of *dilemmas* or *alternatives*, the decision being, in almost all cases, to be made merely between *two opposite* or *obviously distinct* characters. These decisions or *dilemmas* being, moreover, few in number, conduct the student with absolute precision (provided the tables be free from error, and the specimen a good one), to the order or genus to which his plant belongs. . . .

There follows (p. 3–11, Part I) a "Synopsis of the Linnean Artificial Classes" in a bracketed outline form very much like that used by Ray, Rivinus, and Morison—even to the frequent use of adjectives in different series modifying an original noun (Wood's tables were in English, however). Similar bracketed tables are provided for the genera under most "orders" (families).

In his second edition, copyrighted in 1846, Wood altered his key to families to a "Synopsis of the Natural System" (p. 131–136) and placed it in good parallel-type key form, like that first introduced by Lamarck. (Although thus abandoning the Linnaean system in the family key, he neglected on p. 112–113 to modify the remark of p. 108–109 of the first edition that "it has been thought best to retain, in this work, the artificial characters of the Linnaean Classes and Orders, in the form of *analytical tables*. . . .") The tables for genera, although often changed from those of the first edition, remained in bracketed outline form in the second.

Asa Gray, in the first (1848) edition of his *Manual*, also included (p. lxvii–lxxii) a parallel-type "Analytical Key to the Natural Orders of the Plants of

the Northern United States." Its function was clearly indicated (p. xxix): "To assist the learner in practically arriving at the leading characteristics of the orders, while ascertaining the order to which an unknown plant belongs, an artificial analytical key to the orders is appended . . ." This key (perhaps one of the first such tables or analyses called a *key*)* is preceded by a synopsis of the Linnaean system and by a one-page bracketed outline (p. 1) entitled "Synoptical View of the Linnaean Artificial Classes" which is almost identical with a similar outline in Wood's first edition (p. 3, Part II) entitled "Synopsis of the Linnean Artificial Classes." Throughout the remainder of the *Manual*, Gray used only natural synopses of the sort familiar for years in both Europe and America—generally consisting of assorted punctuation marks and symbols dividing the text of a particular genus into natural units. Both Wood and Gray remind us, however, that even the Linnaean system was in its fundamental concept like an artificial key to the flora.

A quite different way of setting up a key is that used for many years by British entomologists and developed extensively by Brig. W. H. Evans of the British Museum in some of his publications on the lepidopterous family Hesperiidae. He gives no instructions whatever for their use, and the student must figure them out for himself. Once one is familiar with the method, it works amazingly well and has the advantage of providing a numbering system which may be used (instead of page, plate, and/or figure numbers) for cross-references and indexing. An illustration from Evans' *Catalogue of the Hesperiidae from Europe, Asia and Australia* will give an introduction to the way in which he frames his keys. Let us assume that the key to "generic groups" (he emphasizes these rather than subfamilies or tribes) has led us to Group J, the *Plastingia* Group. We turn to the key to genera in group J and find the following beginning to the key (p. 32–33; some characteristics omitted):

1a (25a). Hindwing cell not abnormally long.
1b (12a). Antennal apiculus not longer than twice width of club.
1c (5a). H. dorsum not longer than costa.
1d (4). Palpi third segment long and thin.
1e (3). F vein 4 nearer to vein 3 than to vein 5.
1 (2). F vein 1 straight.
Scobura. 7 species. N. India and China to Borneo.
2 (1). F vein 1 more or less bowed.
Suada. 3 species. N. India to Borneo and Philippines.
3 (1e). F vein 4 mid veins 3 and 5.
Suastus. 4 species. India to Borneo and Philippines.
4 (1d) Palpi third segment very short.
Cupitha. 1 species. India to Philippines and Celebes.
5a (1c). H dorsum longer than costa.
5b (10a). F vein 3 opposite vein 9.

* Professor Bartlett has recently reminded me of Linnaeus' key (*clavis*) to the kinds of botanists, which appears in the 1747 edition of his *Bibliotheca Botanica*. (According to Pritzel, this also was in the first edition of 1736.) The "Clavis Classium in Systemate Phythologorum" (at least in 1747) consists of a simple bracketed outline of the classification of botanists which Linnaeus later discusses in the *Bibliotheca*

5c (7a). F vein 5 decurved.
5 (6). Palpi third segment short.
Zographetus. 4 species. N. India to Philippines and Celebes.
6 (5). Palpi third segment long and thin.
Oerane. 1 species. N. India to Borneo and Philippines.
7a (5c). F vein 5 straight.
7 (8a). Antennae not greater than one-half costa.
Hyarotis. 3 species. India, Borneo and Philippines
[and so forth to]
25a (1a). H cell abnormally long. . . . [etc.]

No new number is introduced until a different genus is keyed out; genus 1 is *Scobura*, genus 2 is *Suada*, genus 3 is *Suastus*, etc. We turn to section J-1 of the text to find a key to species of *Scobura*, to section J-2 for a key to *Suada*, etc. Species are similarly keyed, no new number being introduced into the key until it will correspond with a single species. Thus, a reference in the index to J 3/2 means the second species in the third genus of group J. A perusal of the abridged key above, through location of contrasting leads, will demonstrate far better than would a verbal description the method in which such a key is to be used. It is really a good dichotomous key similar to the indented type, but numbered in a unique fashion and not actually indented. The user simply passes below to the next choice until he is sidetracked to a later number in the key.

Ogden (p. 76–86) has proposed a "Selective Key" to those subsections of the genus *Potamogeton* which include the broad-leaved species. Thirty-eight characteristics are arranged in a tabular form so that the user may start with whatever one of them is easily noted on an unknown plant. As Ogden states, the key "is selective in that the user may choose the order in which the characters may be applied. This is of decided advantage when certain parts of the specimen are absent or difficult to make out, for the other parts may be sufficient for determining the subsection." Although the appearance is not at all like the traditional key, this "selective key" certainly qualifies in purpose as a true key.

A light note on the matter of keys has been sounded in A. F. Carr's "The Fishes of Alachua County, Florida. A Subjective Key." Published as the "Carr Key Number" of *Dopeia* (not to be confused with its more respectable ancestor, *Copeia*), the "subjective key" includes delightful leads like "Fish fossil-like, with a patently paleozoic aspect"; "Mouth with a sardonic leer and too many teeth to conceal"; "Fore-and-aft f'ns with spars, or at least with a small jury mast before the m'n t'pf'n." In spite of its subjective nature, occasional iambic pentameter, and dramatic "Act 4" as the result of selecting the first lead in couplet 16, this key, I am told by tolerant zoologists, is one of the best keys to Florida fishes ever published.

Keys are not always limited strictly to the identification of *organisms*. There are examples like Stevenson's parallel-type key to bird nests (1942) and Beard's indented-type analytical key for recognition of tropical American plant formations (1944). A number of biologists have also varied the key by accompanying their leads with sketches or diagrams, rather than segregating these into separate

text figures or plates. Geologists have prepared keys to rocks and minerals. These variations do not represent, however, basic modifications in the mechanics of key preparation.

III. SOME PHYLOGENETIC BACKGROUND

As we leave the story of keys to consider the development of phylogenetic trees, let us consider some of the fundamental ideas of relationship which preceded the actual formation of the first branched family tree. The concept of the fixity of species is worth a brief review.

The Protestant Reformation had removed for its followers the authority of the Church hierarchy, but in substitution laid even greater emphasis on the authority of the Bible and its literal interpretation. It is that situation, and probably the vivid accounts of Milton, which we may properly credit for the idea of special creation. St. Augustine and St. Thomas Aquinas rejected the idea, so it is evident that Catholic theologians had by no means been unanimous in supporting it. Belief in the fixity of species (as the logical result of special creation) was the conception held by great naturalists from Ray and Linnaeus (at least in his early life) down to Cuvier and Louis Agassiz. It did much to obscure the rudimentary notions of organic evolution which had influenced naturalists and philosophers from the time of Aristotle. (Cf. Poulton, p. lxxxv–lxxxvi.)

As was early pointed out by Bartlett (1915, p. 132–133), even Linnaeus came eventually to believe in more species flexibility than he is generally given credit for. His most positive and oft-quoted statements in regard to the immutability of species occur in the *Fundamenta Botanica* and *Philosophia Botanica*. These were precept, however, and not practice. In his actual systematic work after 1753 there are signs that his views became somewhat modified.

> . . . without in any way attempting to read into his statements more than he himself meant we see clearly that his view on the fixity of species changed considerably and that he soon came to believe in the production of new species as well as new varieties by hybridization, by the effect of environment and by cultivation. He removed the statement "nullae species novae" from the preface to the 1766 edition of 'Systema Naturae' and crossed out "Natura non facit saltus" in his own copy of 'Philosophia Botanica'; and we may add that a comparison of some of the specific descriptions in the two editions of 'Species Plantarum' shows that he no longer believed in species being so fixed that they could be differentiated by a single short expression. Much can also be made of his ecological grouping of species and of his recognition of adaptation to environment. (Ramsbottom, p. 216–217.)

It must be remembered that the *Fundamenta* and *Philosophia* were not only published at an early date, but also that as students' textbooks they were likely considered better for containing categorical statements than philosophical speculations. Bartlett (1940, p. 362) has said that "We must recognize that Linnaeus was a forerunner of Darwin to the extent that he believed in the relationship of species and genera by descent," for he had a curious doctrine that "fundamentally distinct types, produced in the beginning by fiat, hybridized by miraculous intervention in an orderly manner in all possible combinations,

which process was repeated by the primary hybrids and then again by the secondary, until the genera and species were produced."

The Swiss-American naturalist, Louis Agassiz, held to the fixity of species with a religious fanaticism. Only a few months before Darwin's *Origin of Species* was brought out, Agassiz published his *Essay on Classification* (1859). In this volume he expresses, among many views, his beliefs that the presence of fossils of all four of Cuvier's main types in the oldest geological formations indicates no ascending scale of life, that "species have fixed characters, and that they do not change in the course of time" (p. 75), and that all taxonomic categories are as natural as the species. In summary, he states:

> All organized beings exhibit in themselves all those categories of structure and existence upon which a natural system may be founded, in such a manner that, in tracing it, the human mind is only translating into human language the Divine thoughts expressed in nature in living realities.
>
> All these beings do not exist in consequence of the continued agency of physical causes, but have made their successive appearance upon earth by the immediate intervention of the Creator. (p. 204–205.)

Agassiz could never accept the momentous theory published by Darwin less than a year later, although his colleague at Harvard, Asa Gray, was prompt to do so. But it is not to Darwin that we turn for the first suggestion of the tree form of expressing phylogeny.

We have referred to Aristotle's "ladder of life"—an idea which was taken up again with the revival of interest in classical learning. "L'Echelle de la Nature" of Bonnet was essentially similar—a single chain or natural series. The idea of species' being arranged like knots on a net was proposed by Donati and was also suggested by Linnaeus: "All plants show affinity on both sides, like a territory on a geographical map."[7] (This idea of affinity appears directly after "*Natura non facit saltus*" in paragraph 77 of the *Philosophia Botanica*.)

In 1764, however, Bonnet, in the third part of his *Contemplation de la Nature*, entitled "Vue Générale de la Progression Graduelle des Etres" (Ch. xx), wrestled with the relationships of the insects and the shell-fish and raised some questions (p. 59):

> Does the scale of nature become branched as it arises?
> Are the insects and the shell-fish two parallel and lateral branches of this great trunk?
> Are the frog and the lizard, so similar to the insects, a ramification of them?
> Do the crayfish and the crab likewise branch off from the shell-fish?
> We still cannot answer these questions.[8]

---

[7] *Plantae omnes utrinque affinitatem monstrant, uti Territorium in Mappa geographica.*

[8] *L'Echelle de la Nature se ramifieroit-elle en s'élevant?*
Les Insectes & les Coquillages seroient-ils deux Branches latérales & parallelles de ce grand Tronc?
La Grenouille *& le* Lézard *si voisins des Insectes, en seroient-ils une Ramification.*
*L'*Ecrevisse *& le* Crabbe *seroient-ils pareillement un Rameau des Coquillages?*
Nous ne pouvons encore satisfaire à ces questions.

This apparently was the first suggestion of a branched tree form as a modification of "L'Echelle de la Nature," but the idea conflicted too greatly with Bonnet's "L'Echelle des Etres" to be pursued seriously. Pallas took up the idea, and Buffon made a sort of synthesis of the tree and the net, in that he regarded the trunk as composed of bundles which at intervals gave off side-branches of bundles, and these united with bundles of another order. (Cf. Bather, p. lxxvii.)

In the 14th volume of his *Histoire Naturelle* (1766), Buffon has a chapter entitled "De la Dégénération des Animaux" in which this idea is put forth:

> . . . the elephant, the rhinoceros, the hippopotamus, the giraffe form simple genera or species which are propagated only in a direct line and have no collateral branches; all the others appear to form families in which one ordinarily notices a principal and common trunk, from which seem to have issued different stems and the more numerous, as the individuals of each species are smaller and more prolific.[9] (p 335.)

He discusses hybrids, suggesting the coming together of related branches to produce a new form. But just as Nehemiah Grew had given suggestions for writing a key, but never wrote one himself, so Buffon and his contemporaries never actually published diagrams of their proposed trees.

IV. TREES AND EVOLUTION

Lamarck again deserves credit for the first actual representation of the object of our attention. In 1809 he published his famous *Philosophie Zoologique*, in the second volume of which he proposed a diagram to illustrate the origins of the major groups of animals. This is reproduced in figure 7. His explanation (p. 462) is as follows:

> The following table will facilitate the understanding of what I have just set forth. One will see there that, in my opinion, the animal scale begins by at least two distinct branches, and that, in the course of its extension, several branches appear to terminate it in certain places.[10]

It should be observed that the earliest proposals for "nets" or "trees" did not include the concept of evolution. They merely diagramed a supposed relationship. Beginning with Lamarck, however, and continuing through Darwin to Haeckel, the concept of a tree included evolution and time in its meaning. Darwin, in a letter written to Asa Gray in 1857, expressed his idea:

> . . . organic beings always *seem* to branch and subbranch like the limbs of a tree from a common trunk, the flourishing and diverging twigs destroying the less vigorous—dead and lost branches rudely representing extinct genera and families. (Darwin & Wallace, p. 53.)

[9] . . . *l'éléphant, le rhinocéros, l'hippopotame, la giraffe forment des genres ou des espèces simples qui ne se propagent qu'en ligne directe & n'ont aucunes branches collatérales; toutes les autres paroissent former des familles dans lesquelles on remarque ordinairement une souche principale & commune, de laquelle semblent être sorties des tiges différentes & d'autant plus nombreuses, que les individus dans chaque espèce sont plus petits & plus féconds.*

[10] *Le tableau suivant pourra faciliter l'intelligence de ce que je viens d'exposer. On y verra que, dans mon opinion, l'échelle animale commence au moins par deux branches particulières, et que, dans le cours de son étendue, quelques rameaux paroissent la terminer en certains endroits.*

Darwin's ideas were quickly developed by Ernst Haeckel, who in 1866 published his *Generelle Morphologie*, in volume two of which he presents eight plates

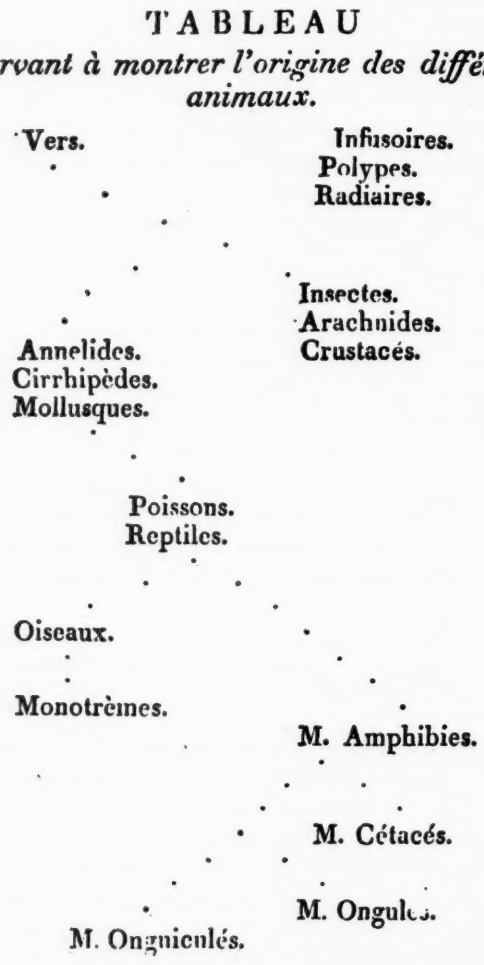

FIGURE 7. The tree published by Lamarck in his *Philosophie Zoologique* (1809, Vol. II, p. 463; figure made from the 1830 reprint), reproduced natural size. The "roots" are at the top of this tree.

of *Stammbaume*. These are often given the credit for being the first genealogical trees; they are at least far more realistic than Lamarck's, for the roots are at the bottom and each diagram is more tree-like. Haeckel's "Stambaum des Menschen" of his 1874 *Anthropogenie* is a famous example of his trees, with all

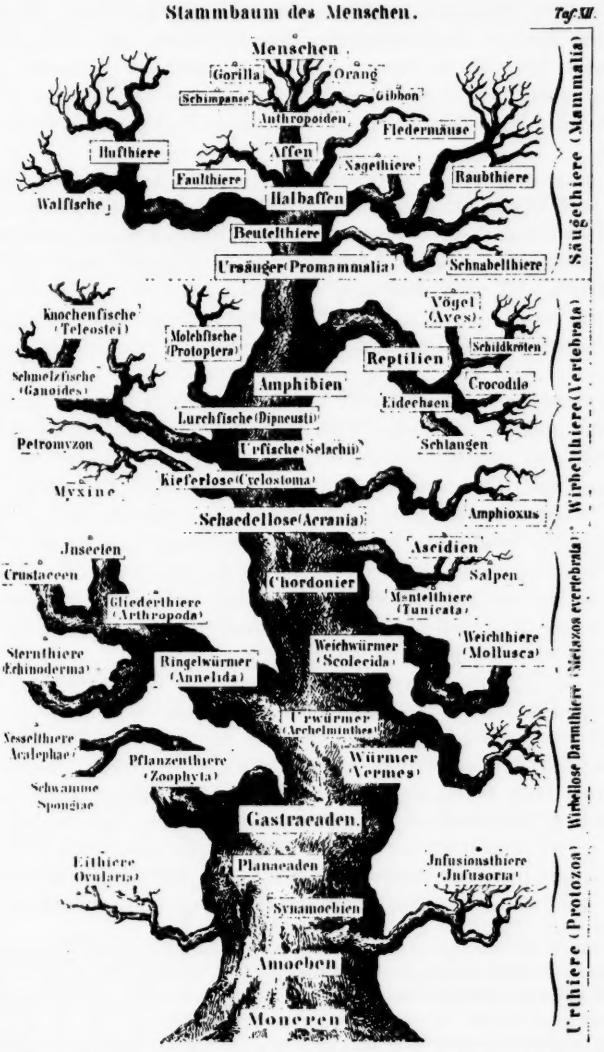

FIGURE 8. Haeckel's "Stambaum des Menschen" from the 1874 *Anthropogenie* (pl. 12, facing p. 496), reduced to three-fourths original size.

the realistic touches of bark, trunk, gnarled limbs, and tiny twigs. Figure 8 reproduces this tree of Haeckel's. It was Haeckel, incidentally, who introduced the term *phylogenie* (*Generelle Morphologie*, p. 57), and he took as his starting point in his *Anthropogenie* the phrase he made famous: "Die Ontogenie ist eine kurze Recapitulation der Phylogenie." (p. 7.)

We have been concerned in this review with the mechanics of tree-like expression and some of the prerequisite ideas of natural philosophy which have borne upon it, not with the history of evolution itself nor the merits or demerits of the relationships expressed by any particular tree. The former and to some extent the latter have been discussed thoroughly by Osborn in *From the Greeks to Darwin.*

Phylogenetic symbols have received particular attention from Lam, whose history of their modification, starting with Haeckel, is so abundantly documented and illustrated that it is only necessary here to refer to his scholarly studies. (Cf. Lam, 1936.) In his paper, Lam discusses 26 different types of phylogenetic symbols (trees and very dissimilar variations thereof)—these certainly have varied more from Lamarck's original than have keys! Figure 9 reproduces one of Lam's own trees, showing how biogeography and paleontology can be integrated.

We can conclude our short survey by alluding briefly to a few recent observations on the question of trees. "With the development of new opinions about the methods and speeds of evolution, the patterns of family trees which are popular as abbreviated and graphic interpretations of phylogenies have been modified," states Jepsen (p. 81), who goes on to discuss some of the specific effects which the results of genetics and paleontology have on the construction of trees. A similar point has been raised by Anderson (p. 225–226) in calling attention to the confusion which amphidiploidy (allopolyploidy) in plants has introduced into phylogenetic diagrams, which then cannot be dendritic but must in some way be more complexly interwoven.

Simpson (p. 259) has presented the viewpoint of the paleontologist that the tree method of expressing phylogeny may be criticized because the present time, supposedly represented by the twigs on the tree, is merely one of an infinite number of possible cross-sections of the history of life. There was no time when there existed only trunk or branches; there have always been species. The adult tree thus represents only present conditions, not history, and a seedling would be a better analogy for past conditions. His conclusion that "no figure that leaves out time can represent history" has also been expressed by Lam (1938a, p. 116) in distinguishing between taxonomy and phylogeny:

> If taxonomical schemes are symbolized by two-dimensional figures in a plane, the Time Factor must be thought perpendicular to that plane. Phylogenetic symbols must therefore make use of three dimensions, one of which is always Time. This Time Co-ordinate which is considered as constant, is crossed by innumerable Time Levels, in each of which a momentary taxonomic scheme may find its place. Phylogeny considers changes from Time Level to Time Level, from taxonomic scheme to taxonomic scheme . . .

It is still a relatively rare phylogenetic chart which actually gives the impression of three dimensions. This has most often been accomplished by a perspective drawing, as illustrated in figure 9, but a given level of the historical tree can also be shown by a separate cross section. This has been done by Schmidt (p. 84–85) for the families and subfamilies of snakes; in two separate figures he provides a branched tree and a series of circles which in cross section represent the trunks and main branches of the tree.

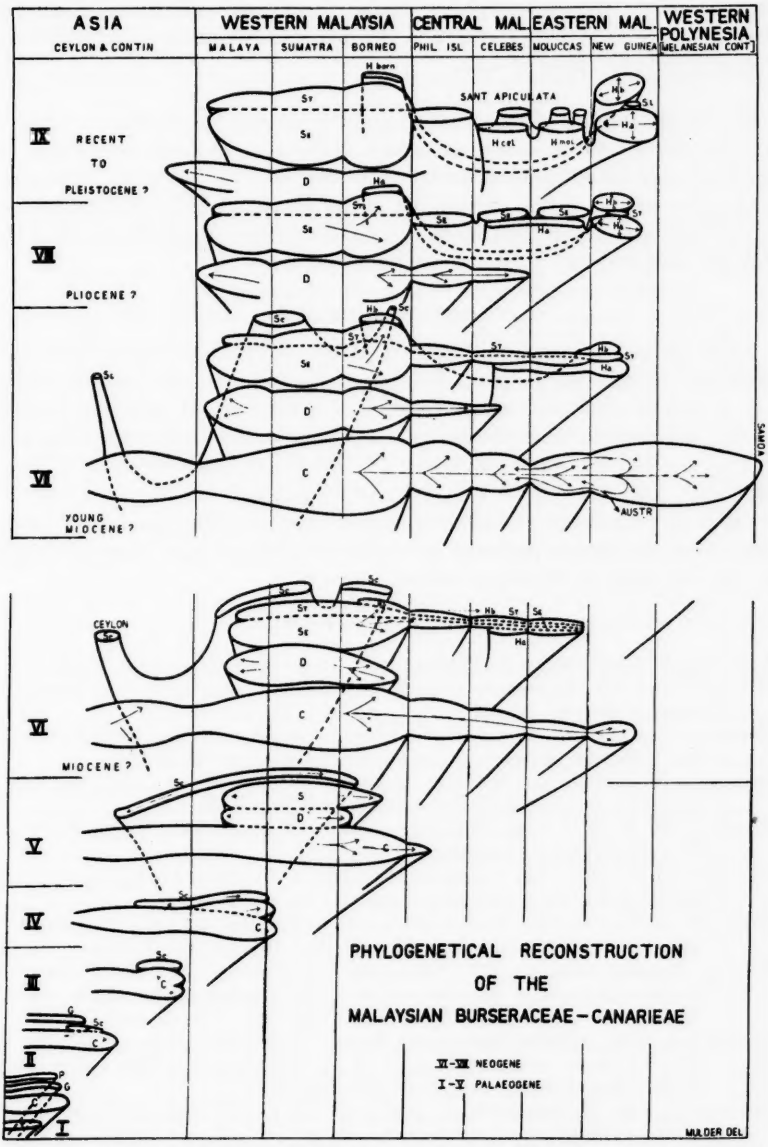

FIGURE 9. A modern tree from the Dutch botanist Lam (1938b, p. 152–153), reproduced slightly over one-half original size. The figure represents the time level, the estimated relative diversity of taxonomic units, and their areas.

Very extensive use of trees, generally of the traditional sort, is made in Gregory's recent *Evolution Emerging* (Vol. II). Most of these are illustrated

with figures in appropriate places among the "branches." Some of his trees show adaptive radiation or evolution of a particular organ or part, rather than the supposed phylogeny of taxa.

The simple notions of classification and the plain ladder of life conceived by Aristotle have become vastly developed. Keys and trees are both firmly embedded today in systematic biology. My own wish to see them in historical perspective has led to the preparation of this essay, which it is hoped will help others who may be curious about the matter to save themselves a long hunt through scattered and often unavailable literature.

ACKNOWLEDGEMENTS

I am deeply indebted to Professor H. H. Bartlett, of the University of Michigan, for his very helpful advice, his criticism of the manuscript, and the use of several volumes from his extensive library of old and rare botanical books. The reproductions in figures 1, 2, 4, and 5 have been made from copies in Professor Bartlett's personal library. To Dr. Pierre Dansereau and Dr. Rogers McVaugh, both also of the University of Michigan, I am likewise grateful for reading the manuscript and offering their suggestions. The figures have all been made from photostats prepared under the direction of Mrs. Alvina Woodford of the University of Michigan General Library.

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A BRIDGE CIRCUIT FOR STUDIES OF NUCLEAR MAGNETIC RESONANCE[1]

ROBERT DONALD SMITH[2]

ABSTRACT

The most accurate values for nuclear magnetic moments have been obtained by studies of nuclear magnetic resonance phenomena at radio-frequencies. This article presents a brief outline of the theoretical interpretations of observed resonance phenomena and describes a bridge circuit developed for the study of the proton resonance. Photographs of the resonance lines obtained under various conditions are shown. The observed line shapes are discussed, and further circuit improvements are suggested.

I. INTRODUCTION

Over a period of years the magnetic properties of the nucleus have been a constant source of interest to the physicist. More recent study of this property of the nucleus has advanced the explanation of the hyper-fine structure of spectral lines. Theories, new experimental methods and improved equipment have made a more thorough investigation possible. Research in this field of physics plays an integral part in obtaining an overall picture of the relationships between the components of an atom. It helps clarify interaction between the nucleus and its associated electrons, in turn, a more accurate determination of the hyper-fine structure of spectral lines is made possible.

At present the nuclear magnetic resonance phenomenon produces the most reliable results and is widely employed by investigators. This thesis presents a study of the shape of the magnetic resonance signal of the proton. A permanent magnet was employed along with a bridge circuit to detect the signal. Such a circuit is advantageous in that it eliminates altering the physical or chemical form of the nuclei contained in the sample to be studied.

II. THEORY

A. Electronic and Nuclear Magnetic Moments

As early as 1891 the fact that some spectral lines may be composed of closely spaced components was suggested in a paper by Michelson (1). Fabry and Perot (2); and Lummer and Gehrcke (3) presented similar articles in 1897 and 1903, respectively. These observations were further substantiated by Janicki (4) in 1909 and Wali-Mohammed (5) in 1914. Originally, explanations of this hyper-

[1] Submitted in August, 1952.

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fine structure were in terms of the effects produced by the differences in atomic mass in the nuclei of various isotopes of each element. Although this "isotope effect" accounted for a small number of the hyperfine structure lines in some of the spectra, it did not account for all the hyperfine structure of all the lines in the observed spectra. These additional effects were explained by Pauli (6) in 1924 on the assumption that the nucleus was spinning. For a given electronic state such a spinning nucleus gives rise to slightly separated energy levels. These closely spaced energy levels cause the hyperfine structure of spectral lines. The spinning nucleus also possesses an angular momentum and an associated magnetic moment.

An atom may be pictured as consisting of a charged nucleus about which spinning electrons execute orbital motion. The angular momenta of these charged

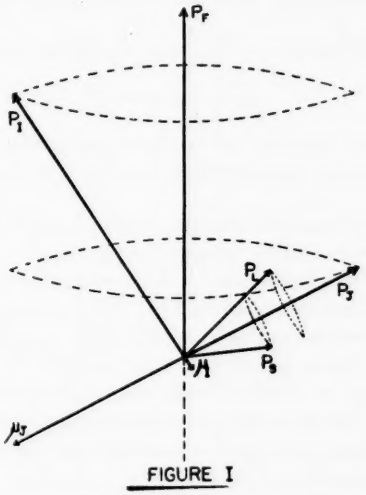


FIGURE I

particles may be represented vectorially by the vector model in Figure I (7). The vectors p_S and p_L represent the total momenta due to the spin and orbital motion of all extranuclear electrons, respectively. These two vectors combine to give the resultant angular momentum of the electrons p_J, with an associated magnetic moment μ_J. The vector p_I represents the angular momentum of the spinning nucleus, with an associated nuclear magnetic moment μ_I. The total angular momentum of the extranuclear electrons is coupled with the nuclear angular momentum to form the resultant angular momentum of the atom p_F.

For an atom having one extranuclear electron, quantum mechanical analysis shows that the angular momentum due only to orbital motion of the electrons has the magnitude:

$$p_l = l^* h/2\pi \qquad \text{where} \qquad l^* = \sqrt{l(l+1)},$$

l being the azimuthal quantum number. The magnetic moment μ_l due to this orbital motion is essentially that of a moving charge or current $i = e/T$, where e is the electronic charge and T the period of revolution. The magnetic moment is therefore predicted classically to be:

$$\mu = (A \cdot i)/c \qquad \text{(I)}$$

where c is the velocity of light and A is the area of the circuit.

The area of the circuit is the area of a Kepler ellipse[3] in terms of the electronic mass m, its orbital angular momentum p, and the period T. This area is given semi-classically as:

$$\text{area} = A = |\,(T/2m)p\,| = (T/2m)(l^*h/2\pi),$$

since the angular momentum associated with orbital motion of an electron is $p_l = l^*h/2\pi$.

Substitution of the values for the current and area into Equation I gives:

$$\mu_l = (eh/4\pi mc)l^*,$$

which is the magnetic moment due only to the orbital motion of an electron. The constant term in this expression $(eh/4\pi mc)$ is termed the Bohr magneton (μ_B).

The angular momentum of a spinning electron is found by quantum mechanical methods to be: $p_s = s^*h/2\pi$, where $s^* = \sqrt{s(s+1)}$ and s is the spin quantum number which has the value $\frac{1}{2}$. The magnetic moment associated with this spin angular momentum is found to be twice as large as the semi-classically predicted value. The required correction may be supplied by assuming a correction factor, the Landé g-factor. For an electron describing orbital motion only, the factor is $g_{l^*} = 1$; for a "spin only" electron, the factor is $g_{s^*} = 2$; for an electron having both spin and orbital angular momenta, g has a value between 1 and 2. Thus, the magnetic moment of a "spin only" electron may be expressed as $\mu_s = g_{s^*}\mu_B s^* = 2(eh/4\pi mc)s^*$.

In studying the spatial orientations of the magnetic moment vectors, it is necessary to establish a unique reference direction. This is done by applying an external magnetic field. In this field, the spin and orbital motions of a single electron assume quantized orientations in space, resulting in an electronic magnetic moment of magnitude.

$$\mu_j = g_j m_j \mu_B\,, \qquad \text{(II)}$$

where g_j is the Landé g-factor for the electron, and where m_j is the magnetic quantum number, which is the projection of the resultant quantum number $j = |\,l \pm s\,| = |\,l \pm \frac{1}{2}\,|$ onto the direction of the field. In a corresponding manner, the electronic magnetic moment of an atom having more than one electron may be expressed as $\mu_J = g_J m_J \mu_B$, where J is the total electronic quantum

[3] The Kepler ellipse describes the motion of a planet sweeping a constant area per unit time in stellar space and is applicable to the motion of the electron within an atom.

number and is given by $J = (L - S) \cdots (L + S)$ if $L \geqq S$ or $J = (S - L) \cdots (S + L)$ if $S \geqq L$. In this expression L and S are the total electronic orbital and spin quantum numbers, respectively. The total angular momentum of the nucleus resulting from the orbital and spin momenta of its constituent particles is analogous to the total angular momentum of the electrons and must be represented by $p_I = I^*h/2\pi$. The magnetic moment associated with this nuclear angular momentum would be classically predicted to be:

$$\mu_I = (eh/4\pi Mc)I^*,$$

where M is the mass of the proton, e the proton charge and $I^* = \sqrt{I(I+1)}$ is the effective nuclear quantum number. The constant term, $(eh/4\pi Mc)$ is termed the nuclear magneton, μ_N corresponding to the Bohr magneton. As with the electronic magnetic moment, this classical prediction is found to require a correction factor. In the case of the nucleus, this correction is referred to as the nuclear g-factor, g_I, and is given by the ratio of the nuclear magnetic moment in nuclear magnetons to its angular momentum. The corrected equation for the nuclear magnetic moment is thus:

$$\mu_I = g_I I^* \mu_N . \tag{III}$$

In establishing the vector properties of the nuclear magnetic moment, an external magnetic field is required for a reference direction, just as in the case of the electronic magnetic moment. In such a field then, the component of the nuclear magnetic moment parallel to the applied field is:

$$\mu_H = g_I m_I \mu_N$$

where m_I is the projection of the nuclear spin quantum number I onto the field direction and has the values $I, I-1, \cdots, -I+1, -I$.

The total magnetic moment of an atom is formed by combining the orbital and spin magnetic moments of the electrons with the nuclear magnetic moment. Due to the fact that the mass M of a proton is about 1840 times as large as the electronic mass m, the nuclear magneton is much smaller than the Bohr magneton, and, as a first approximation, the nuclear magnetic moment may be neglected. Thus, the orbital and spin motions of the electrons roughly determine an atom's resultant magnetic moment μ_J. The existence of this atomic magnetic moment was verified by Stern-Gerlach (8) through their atomic-beam experiments in 1921.

In most molecules the valence or outer electrons of the constituent atoms are exchanged with the valence electrons of the other constituent atoms to form closed electronic shells with the total electronic magnetic moment equal to zero. Thus, the resultant magnetic moment for a molecule will be determined by the nuclear magnetic moment μ_I. The molecular-beam experiments of Frisch and Stern (9) and Rabi (10) in 1933 and 1934, respectively, confirmed the existence of a nuclear magnetic moment. More accurate measurements of the nuclear magnetic moment have been obtained by using the nuclear magnetic resonance method.

When placed in a strong magnetic field of several thousand gauss the nuclear magnetic moment assumes definite quantum mechanically predicted orientations with respect to the direction of the applied field H_0. The spins of the nuclei interact with the external magnetic field, causing a precession of the total magnetic moment about the direction of the external field. The torque producing this precession is given by:

$$L = \mu_I \times H_0 .$$

The value of the nuclear magnetic moment is seen to be $\mu_I = \gamma p$, where γ, the gyromagnetic ratio, is given as $\gamma = (ge/2Mc)$ and $p = (I^*h/2\pi)$. The rotational analogue of Newton's law shows $(dp/dt) = L$, where p is the angular momentum of the system. Thus:

$$L = (dp/dt) = -\gamma H_0 \times p.$$

This expression is recognized to be the equation of motion of a vector p precessing with a rotational velocity $\omega_0 = -\gamma H_0$, so that $dp = \omega_0 \times p\, dt$. The rotational velocity of this precession is termed the Larmor precessional velocity and is seen to be $\omega_0 = (-g\mu_N H_0 2\pi)/h$, where μ_N is the nuclear magneton. This velocity may be written as $\omega_0 = 2\pi\nu_0$, where ν_0 is the Larmor precessional frequency in cycles per second and is given by:

$$\nu_0 = (g\mu_N H_0)/h. \qquad \text{(IV)}$$

When the applied field (H_0) has a magnitude of several thousand gauss, the value of the Larmor precessional frequency is in the radio-frequency range. Thus, if a magnetic field which is rotating or oscillating at the Larmor frequency is oriented perpendicularly to the applied field H_0, the precessing nuclei should produce an observable effect on the radio-frequency field—either a slight power loss or a slight phase shift. As in a tuned circuit, this phenomenon occurs at only one frequency and is therefore, referred to as a nuclear magnetic resonance phenomenon.

Measurements of nuclear magnetic moments are obtained by using a macroscopic sample of molecules containing the desired nuclei. This sample is placed in a magnetic field of several thousand gauss and a radio-frequency field satisfying the Larmor condition is applied perpendicularly to the main external field (H_0). Whenever the Larmor conditions as given by Equation IV are satisfied, the effects of the precessing nuclear magnetic moments are observed as changes in the electrical conditions of a tank circuit which is in the radio-frequency or r-f field. In most cases the r-f field is tuned to a frequency which satisfies the Larmor conditions and then held constant. The applied field H_0 is then varied by modulating or superposing on it a small sinusoidal field H_1. This varying field periodically satisfies the Larmor conditions so that the nuclear resonance phenomenon occurs as shown in Figure II. The line AA' represents the value of the magnetic field required to satisfy the Larmor condition at the frequency of the r-f field. When the changing magnetic field passes through these values, the effect of the precession of the magnetic moments will be noted as an energy loss

or phase change of the r-f field. The effect is shown in the figure as a decrease in the energy of the r-f field. This corresponds to the absorption of r-f energy at the Larmor condition by the precessing nuclei.

B. Nuclear Magnetic Resonance Line Shape

The nuclear magnetic resonance phenomenon does not produce an infinitely narrow line but produces a signal that has a definite width. In studying the line shape a knowledge of two interactions will be required, namely the spin-lattice and the spin-spin interactions.

To explain the spin-lattice interaction a sample is assumed to be composed of a framework or lattice network capable of absorbing energy. This lattice represents all the degrees of freedom other than the spin of the nuclei. From quantum mechanics it is known that in an external field there are $2I + 1$ energy levels which the nuclei may occupy. When these nuclei are in the small mag-

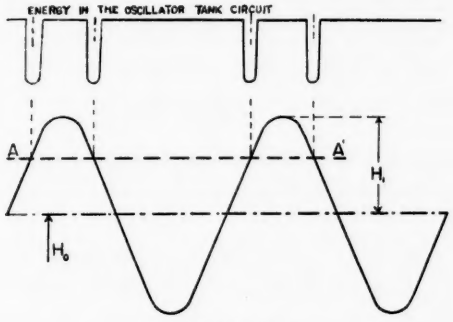


FIGURE II

netic field of the earth, the $2I + 1$ levels are very nearly equally populated. This same situation is true at the first instant the nuclei are thrust into a strong magnetic field of, say, 10,000 gauss. In such a strong magnetic field, the population of the higher energy levels gradually decreases, while that of the lower levels increases. After a short time, an excess population exists in the lower levels. Due to this greater population some of the nuclei must therefore lose energy. This energy is withdrawn from the nuclei by some mechanism to a heat reservoir until equilibrium has again been restored. The mechanism by which the energy is transferred is a type of Brownian motion (11). The heat reservoir referred to is represented by the crystal lattice. Theoretically, an infinite time is required for equilibrium to be reëstablished. Arbitrarily, the time needed for all but $(1/e)$ of the excess population to reach the lowest energy level and thus reëstablish equilibrium is defined as (T_1), or the spin lattice relaxation time. This interaction between the spinning nuclei and the lattice is one of the factors which causes broadening of magnetic resonance lines.

The spin-lattice relaxation time can be found quantitatively as follows. Let U_p and U_q represent the energies of the upper and lower states, respectively,

$W(p \rightarrow q)$ the probability of a transition from the p level to the q level and $W(q \rightarrow p)$ the probability of a transition from the q level to the p level. At equilibrium,

$$N(p)W(p \rightarrow q) = N(q)W(q \rightarrow p),$$

where $N(p)$, $N(q)$ are the populations of the two levels. In a magnetic field these populations are governed by the Boltzmann factors. Hence,

$$\frac{W(p \rightarrow q)}{W(q \rightarrow p)} = \frac{N(q)}{N(p)} = \exp\,(U_p - U_q)/(kT),$$

where k represents the Boltzmann constant and T the absolute temperature of the system.

The probability of a single transition from p to q is independent of the population of q and is given by the quantum-mechanical probability $P(p \rightarrow q)$. The total probability W must, therefore, be proportional to the quantum-mechanical probability P, through the Boltzmann factor, giving:

$$W(p \rightarrow q) = P(p \rightarrow q) \exp\,(-U_p/kT),$$

where $U = -\mu_I \cdot H_0 = -\mu_B H_0 = -g(eh/4\pi Mc)m_I H_0 = -g\mu_B m_I H_0$, as shown in Appendix I.

Taking the case where $I = \frac{1}{2}$ and letting N be the total number of spins with $N(+)$ and $N(-)$ in the lower and upper energy states, then, since $P(+ \rightarrow -) = P\,(- \rightarrow +) = P$,

$$W(+ \rightarrow -) = P \exp\,(-\tfrac{1}{2}g\mu_N H_0/kT)$$
$$W(- \rightarrow +) = P \exp\,(+\tfrac{1}{2}g\mu_N H_0/kT)$$

If n represents the excess population in the lower state, then $n = N(+) - N(-)$ and changes by a factor 2 for each transition. The change in the excess population (dn) per unit time (dt) is thus:

$$dn/dt = 2N(-)W(- \rightarrow +) - 2N(+)W(+ \rightarrow -).$$

At room temperatures, n is much less than N. Therefore, the total probabilities may be written as:

$$W(+ \rightarrow -) = P(1 - \tfrac{1}{2} \mid g \mid \mu_N H_0/kT);$$
$$W(- \rightarrow +) = P(1 + \tfrac{1}{2} \mid g \mid \mu_N H_0/kT).$$

Thus,

$$dn/dt = 2P[N(-) + N(-)\tfrac{1}{2} \mid g \mid \mu_N H_0/kT - N(+) + N(+)\tfrac{1}{2} \mid g \mid \mu_N H_0/kT],$$

or

$$dn/dt = 2P(n_0 - n),$$

where n_0 is the excess population in the lower levels at equilibrium and is given by $n_0 = Ng\mu_N H_0/kT$.

Integration of dn/dt with respect to time (t) gives:

$$n = n_0[1 - \exp\,(-2Pt)].$$

From this expression it may be seen that the time required for all but $(1/e)$ of the excess population to reach the lower energy level is $t = 1/(2P)$. This characteristic time is the spin-lattice, or longitudinal, relaxation time (T_1). Thus, $T_1 = 1/(2P)$. This is the time required for the lower energy levels to gain an excess population, resulting in the possibility of nuclear magnetic resonance absorption.

Purcell (11) in 1948 divided the spin lattice relaxation time into two components, one due to the proton's immediate partner $(1/T_1)p$, and the other due to the effect of the neighboring nuclei $(1/T_1)n$. His equation for the total relaxation time is, therefore:

$$1/T_1 = (1/T_1)_p + (1/T_1)_n .$$

For water at 20°C., the value of $(1/T_1)_p$ was calculated to be .19 sec^{-1}; the calculated value of $(1/T_1)_n$ was .10 sec^{-1}. The predicted total relaxation time was thus $T_1 = 3.4$ sec. The value of T_1 for the protons contained in a sample of water was experimentally found by Hahn (12) to be 2.33 ± 0.07 sec. This value agrees in order of magnitude with Purcell's theoretical calculation. The discrepancy may lie either in the theoretical assumptions required to simplify the actual problem or in small experimental errors.

The second principal interaction which affects the shape of the nuclear magnetic resonance line results from a coupling between adjacent nuclear magnetic moments. An individual precessing nucleus in a sample has other precessing nuclei as its neighbors, each of which may be in any one of the available $2I + 1$ energy levels. The net effect of these neighboring nuclei produces a small changing magnetic field. If the nucleus is in an applied magnetic field H_0, the values of the field at the nucleus in question will fluctuate slightly above and below the value H_0. By taking the distances between neighboring nuclei to be r and the net field produced by the neighboring nuclei to be $H_{\text{loc.}}$, the effect of the neighboring nuclei may be approximated by $H_{\text{loc.}} \sim \mu_I/r^3$, where μ_I is the magnetic moment of a single nucleus. By assuming the distances between the nuclei to be approximately one Angström, the local field is seen to be about 5 gauss (14). This variation, when superposed on the applied field, H_0, produces fluctuations in the Larmor precessional velocity of the order of:

$$\delta\omega_0 \sim (g u_N 2\pi/h) H_{\text{loc}} \sim 10^4 \text{ sec}^{-1},$$

or

$$\frac{1}{\delta\omega_0} \sim 10^{-4 \text{ sec.}} (14).$$

For a field of 10,000 gauss, the Larmor precessional velocity is approximately $\omega_0 = 2.67 \times 10^8$ sec^{-1}, and the change in Larmor frequency condition due to neighboring magnetic moments is thus about one part in 10^4 for a field of 10,000 gauss.

Another effect due to the proximity of other nuclei is that two anti-parallel nuclear magnetic moments may induce transitions in each other. That is, if

identical nuclei A and B are precessing about the applied field at exactly the same frequency and if they are anti-parallel, A may induce a transition in B. Then A itself must undergo a transition to the state that B initially occupied. The total effect is that nuclei A and B interchange energy states with no net energy change of the spin system; this is termed a "spin-spin collision". As in the preceding paragraph, the range or spread of the Larmor precessional velocity is represented by $\delta\omega_0$. During the time $1/\delta\omega_0$, the relative phase between two neighboring spins varies appreciably and the nuclear moments of A and B precess with exactly the same frequency for at least one instant so that a spin-spin collision may occur. The time may thus be termed the lifetime of a spin state and is found to be $1/\delta\omega_0 \sim 10^{-4}$ sec. (13).

The combination of these two phase-destroying processes, the local field dispersion and the spin exchange, is the second of the two principal factors that broaden magnetic resonance lines. The characteristic time for the phase to be destroyed is termed the spin-spin or transverse relaxation time and is denoted by T_2.

Though the spin-spin interaction chiefly determines the line width, there are five additional phenomena which contribute to the line broadening.

(1) A magnetic resonance line due to an isolated spinning nucleus has what is termed a "natural width", which results from the fact that the transition probability for the magnetic moment of the isolated nucleus at any time does not permit an infinitely sharp resonance. Pake (13) shows this "natural width" to be given by:

$$\Delta\omega/\omega_0 = \theta = \tan^{-1}(H_1/H_0) \sim H_1/H_0 .$$

(2) The applied magnetic field H_0 may not be uniform over the entire surface of the pole faces. Imperfections in the material used in the pole pieces, such as stresses or impurities, as well as nicks and scratches on the surface of the pole faces, will introduce these inhomogeneities. At best, the variation in the field strength may have a range of 0.5 gauss or more over a surface area of 1 cm^2 in a field of 10,000 gauss. These small variations are negligible, providing care is taken in the construction and handling of the pole pieces. The broadening due to field inhomogeneities may be minimized by using samples which have a small cross sectional area in the direction of the pole faces.

(3) Under certain conditions, the spin-lattice relaxation mechanism defined previously may determine the lifetime of a nuclear spin state. From Heisenberg's uncertainty condition, this lifetime results in an energy spread of $\delta U \sim h/(2\pi T_1)$, which, according to the Bohr condition, would spread the resonance frequency over a range $\delta\omega \sim U2\pi/h \sim 1/T_1$. A typical broadening due to this effect is about 1/30 gauss, which is less than the spread caused by field inhomogeneities.

(4) When saturation is reached or when there is no longer an excess population in the lower energy levels, the width at the half maximum intensity, or the "half-width", of the resonance line increases. Saturation is caused by the r-f field supplying more energy to the nuclei than the amount they are capable of dissipating through the relaxation process. The result of this is that the upper

levels have such populations that transitions to them are no longer probable, and absorption may no longer be observed. This broadening, which will be shown quantitatively later, can be reduced to the extent that it may be neglected by operating the r-f field considerably below the point of saturation.

(5) There may also be a quadrupole broadening; that is, the precessing nuclear magnetic moment in a sample may interact with the electric field inside the molecule. Such interactions broaden the line greatly. However, this phenomenon is nonexistent in the cases of the proton.

An analysis of the actual shape of the nuclear magnetic resonance line is given by the Block theory (14). Bloch assumes the Curie susceptibility equation to be true in nuclear magnetic resonance phenomena. The Curie susceptibility equation gives

$$M = \chi H_0 , \tag{V}$$

as in the macroscopic case. In this expression, H_0 is the applied external field, M the magnetic moment per unit volume of the sample, and χ the magnetic susceptibility. The nuclear magnetic moment per unit volume can be found by assuming the nuclei to be characterized by the quotient of its potential energy, divided by kT. This gives the dimensionless exponent of the Boltzmann factor, $\alpha = (g_I \mu_H H_0)/(kT)$. The volume density of the magnetic dipole moments, M_H, must then be:

$$M_H = \sum_{m=-I}^{I} N(m)\mu_H(m) = K \sum_{m=-1}^{I} \exp(m\alpha) g\mu_N m,$$

since $N(m)$ is the number of nuclei occupying the m^{th} energy level and is given by $N(m) = N \exp[-U(m)/kT]$, where $U(m)$ is the potential energy of the m^{th} energy level. For a given nucleus, the constant is much less than unity. By means of the normalization condition:

$$N = \sum_{m=-I}^{I} N(m) = \sum_{m=-I}^{I} K \exp(m\alpha),$$

K is found to be equal to $N/2I + 1)$. Therefore:

$$M_H = \frac{N}{2I+1} \sum_{-I}^{I} (1 + \alpha m)\alpha \frac{kT}{H_0} m = \frac{N}{2I+1} \alpha^2 \frac{kT}{H_0} \sum_{-I}^{I} m^2$$

but

$$\sum_{-I}^{I} m^2 = 1/3I(I+1)(2I+1)H_0$$

From equation (V), the Curie susceptibility of the nucleus may be shown to be

$$\chi_n = (N/3kT)g^2\mu_n{}^2 I(I+1).$$

This susceptibility is composed of a real and an imaginary component, and may be represented by $\chi = \chi' - i\chi''$. The real component of the product of $\chi = \chi' - i\chi''$ and $H_{\text{osc}} = 2H_1 \exp(i\omega t) = 2H_1 (\cos \omega t + i \sin \omega t)$ is thus seen to be:

$$M = \chi'(2H_1 \cos \omega t) + \chi''(2H_1 \sin \omega t). \tag{VI}$$

Equation (VI) may be derived by assuming the applied magnetic field H_0 to be parallel to the Z axis of an orthogonal coördinate system and the oscillating or r-f magnetic field H_1 to be parallel to the x-axis with a magnitude of $H_x = 2H_1 \cos(\omega t)$. The resultant oscillating magnetic field may be expressed as a sum of two rotating fields, one rotating clockwise and the other counterclockwise, giving:

$$H_x^{cw} = H_1 \cos \omega t; \qquad H_x^{ccw} = H_1 \cos \omega t;$$
$$H_y^{cw} = H_1 \sin \omega t; \qquad H_y^{ccw} = -H_1 \sin \omega t;$$
$$\text{or } H_{osc} = 2H_1 \exp(i\omega t).$$

From equation (VI) it may be seen that the imaginary component of the product cannot be observed since the applied field is $2H_1 \cos \omega t$. The out-of-phase component of this applied field is measured by the imaginary portion of the susceptibility. The fact that the observed absorption line may be represented by this out-of-phase component is established by consideration of the equation for the hysteresis losses. The magnetic absorption by the nucleus in a sample is assumed to correspond to absorption in a transformer core. The equation for hysteresis losses gives the energy (A) absorbed by a unit volume of the sample per second as:

$$A = \frac{\omega}{2\pi} \int_{t=0}^{t=2\pi/\omega} H \cdot dM$$

By taking the value $M = \chi'(2H_1 \cos \omega t) + \chi''(2H_1 \sin \omega t)$ and assuming M and dM/dt to be colinear with $2H_1$ the energy absorbed is:

$$A = 2H_1^2 \omega \chi''.$$

Bloch found the real and imaginary portions of the susceptibilities to be:

$$\chi' = \tfrac{1}{2}\chi_0 \omega_0 T_2 \frac{T_2(\omega_0 - \omega)}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma^2 H_1 T_1 T_2};$$

$$\chi'' = \tfrac{1}{2}\chi_0 \omega_0 T_2 \frac{1}{1 + T_2^2(\omega_0 \omega)^2 + \gamma 2H_1^2 T_1 T_2}.$$

If the oscillating r-f field is assumed to be lower than the saturation value, there is an excess population of nuclei in the lower energy levels. The saturation factor $\gamma^2 H_1^2 T_1 T_2$ is much less than unity, and the above expressions may be very closely approximated by:

$$\chi' = \tfrac{1}{2}\chi_0 \omega_0 T_2 \frac{T_2(\omega_0 - \omega)}{1 + T_2^2(\omega_0 - \omega)^2};$$

$$\chi'' = \tfrac{1}{2}\chi_0 \omega_0 T_2 \frac{1}{1 + T_2^2(\omega_0 - \omega)^2}.$$

When plotted, these two functions give the curves shown in Figure III (13). The absorption curve is recognized as being represented by Figure IIIB. It is of interest to note that, if the applied external field H_0 is perfectly homogeneous,

the value of $1/T_2$ can be found from the width at half-maximum intensity of the resonance absorption line. From the equation representing χ', the half-maximum intensity is seen to occur when $T_2(\omega_0 - \omega) = 1$, or $1/T_2 = (\omega_0 - \omega)$.

Since the absorption line is a representation of the out-of-phase component of the susceptibility, the in-phase portion of the oscillating magnetic field must represent the real part of the susceptibility. This susceptibility is represented by the dispersion curve shown in Figure IIIA.

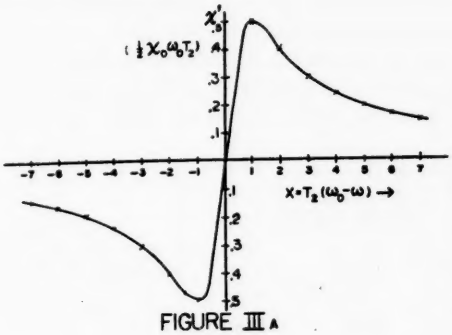


FIGURE IIIA

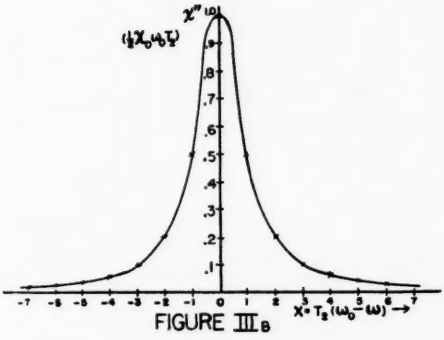


FIGURE IIIB

III. BRIDGE CIRCUITS

The effect of the precessing nuclear magnetic moments is observed in the variations of the energy in the applied radio-frequency field. This field is oriented perpendicular to a strong homogeneous magnetic field of several thousand gauss. In most applications, the magnetic field strength periodically passes through the value satisfying the Larmor conditions. The cyclic variations in field strength due to the precessing nuclear magnetic moment may then be observed on an oscilloscope trace.

Since the time of the original atomic- and molecular-beam experiments (8, 9, 10) four general types of circuits have been developed for observing nuclear magnetic resonance lines using gross matter as samples. These four general categories are 1) the bridge circuits as used by Purcell and Pound and later by

Thomas and Huntoon, 2) the nuclear-induction method employed by Block, 3) the oscillator detector which Roberts and Pound devised, and 4) the radio-frequency-pulse method created by Torrey. The first of these, the bridge circuit, will be discussed in detail here.

The essential feature of any bridge circuit is the use of two identical tuned tank circuits, both tuned to the resonance frequency. The sample is placed within one tank which is located in a strong magnetic field; the other tank, the dummy tank, merely provides a balance. Either a phase or an amplitude balance can be achieved by adjusting the dummy tank.

The bridge circuit developed by Bloombergen, Purcell and Pound in 1948 was an outgrowth of a successful resonating-cavity experiment (15). Their circuit has been the basis for most subsequent work employing bridge circuits.

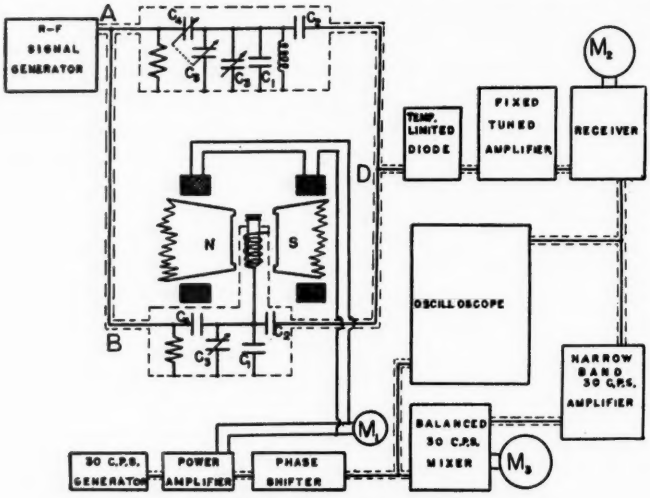


FIGURE IV

The experimental arrangement used by the Purcell group is shown in Figure IV (11). The sample tank was placed in the magnetic field as shown, with the dummy tank well away from the strong magnetic field and separated electrically by a half-wave-length cable.

In operation the r-f signal from a General Radio 805-C signal generator was applied directly to the dummy parallel tank circuit and through the half-wave-length 50-ohm coaxial cable to the sample tank located within the magnetic field. This half-wave-length cable made the output of the bridge circuit at point D a voltage node. The bridge could then be balanced in phase or amplitude by adjusting one of the trimming condensers C_3 and the coupling condenser C_4 in the dummy tank. C_4 and C_5 are "ganged" so as to leave the total tuning capacity unaltered, since the coupling adjustment of C_4 affected the phase balance as well as the amplitude balance. This procedure gave orthogonal phase and amplitude adjustments so that either the absorption curve, involving essentially a

change in the shunt resistance of the sample tank, or the dispersion curve resulting from a slight shift in the natural frequency of the sample tank circuit, could be observed. As a rule the tanks were never completely balanced, but were unbalanced so that the voltage at D was large compared with the change in this voltage as a result of the resonance phenomenon.

The change in the amplitude of the r-f signal due to nuclear resonance effects was amplified by means of a tuned r-f amplifier. A commercial receiver was used as a detector. The detected signal, the 30 cycles per second field modulation frequency, was then superposed in the proper phase with the modulation signal. The balanced 30 cycles per second mixer is a phase detector which has an extremely narrow band pass. The amplitude of the detected signal from the mixer is proportional to the rate of change of either the real or imaginary sus-

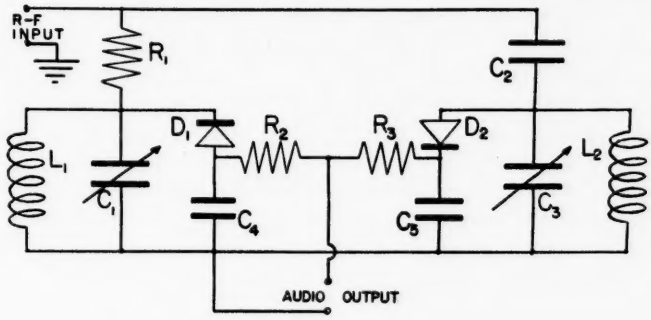


FIGURE V

R_1 = 25000 Ω
R_2, R_3 = 50000 Ω
C_1 = 120 μμfd.
C_2 = 2 μμfd.
C_3 = 7 μμfd. ceramic trimmer
C_4, C_5 = 500 μμfd.
L_2 = 1 μh. r-f choke
D_1, D_2 = 1N38 crystal diodes

ceptibility with respect to the change in the magnetic field strength. The reading of meter M_3 is thus proportional to the slope of the resonance signal. These readings were then plotted versus the frequency, giving the line shape. Purcell *et al.* used this method of observing the line shape since most of their work involved broad, weak resonance lines. In this method, the modulating field is kept at a small fraction of the resonance line width. The meter reading is thus the slope of the line over a small segment. The r-f is then adjusted from the lower frequency limit of the resonance line to the upper limit in small frequency increments. The plot of the meter readings with their corresponding frequency gives the resonance line shapes.

Thomas and Huntoon (16) in 1949 used a variation of the Purcell bridge circuit. In their circuit the modulated r-f signal was detected at the bridge by a crystal diode in each tank circuit. Figure V shows a schematic diagram of their

circuit. When the Larmor conditions are satisfied, the absorption or dispersion effects of the nuclei modulate the r-f signal only in the sample tank. Thus, the audio component appears at the output of the bridge circuit. This signal is then amplified and applied to the vertical deflecting plates of an oscilloscope. If the oscilloscope sweep frequency is the same as the magnetic field modulation frequency the trace appearing on the oscilloscope screen is a reproduction of the resonance line.

A pair of low-impedance series-tuned tanks was used in a circuit by Grivel, Soutif and Buyle (17), replacing the high-impedance parallel tanks used by the Purcell and Thomas groups. Again the sample was placed in one tank; the other tank was merely a dummy, making a balance possible.

The advantage of bridge circuits is that voltage variations in the radio frequency from the r-f signal generator are balanced out with no harmful effect to the resonance signal. This property reduces the need for a highly stable r-f signal generator output voltage. Either the absorption or the dispersion effect of the nuclear magnetic resonance signal can be obtained with properly designed bridge circuits. The presence of either one or the other is highly desirable in any quantitative study. A combination of these two effects may appear, giving an asymmetrical shape to the resonance line. This is of no consequence in studies involving the Larmor precessional frequency of the nuclear magnetic moment. For studies involving line shapes, the pure absorption or dispersion curve is required.

IV. THE MAGNET

The purpose of the present work was to design a bridge circuit suitable for the detection of the proton magnetic resonance signal using a permanent magnet for the applied field.

The magnet used in conjunction with this experiment is of interest because it is one of the largest permanent magnets yet constructed. Figure VI shows the design and dimensions of the magnet's principal components. The magnet was constructed in the Ohio State University Physics Department's shop. It is composed of 12 Alnico V pieces fitted together and clamped into place by four threaded rods, with an inside tapered ring fitted over the pole pieces. The pole pieces are made of soft iron 6″ in diameter, and the gap between them is $1\frac{9}{32}$ inches. The yoke is made from 3″ × 12″ cold-rolled iron stock and is bolted at the corners as shown. A total of 150 turns of number 8 copper wire were wrapped around the magnet. With 69 iron "keepers" inserted in the gap the magnet was "flashed" several times by a current of 800 amperes, giving a magnetizing field of 120,000 ampere turns.

The modulating coils of approximately 1734 turns each are mounted on the retaining rings at the pole faces, as shown in Figure VI.

V. EXPERIMENTAL APPARATUS

It was necessary to know the field strength of the permanent magnet so that the two tanks in the bridge circuit could be constructed in such a way that it

would be possible to tune through the Larmor frequency conditions. The first approximation to the field strength was found by using a fluxmeter which had an accuracy of $\pm 15\%$. An oscillator detector circuit was then used to locate precisely the proton resonance line in this range. Since the oscillator detector consists of only one tuned tank, it is more convenient to use in searching for the proton resonance line than the bridge circuit, which has two tanks. The circuit and operation of this oscillator detector are described in detail in the thesis of James C. Gilfert (18). From the value of the Larmor frequency, the field strength was calculated to be 7800.6 ± 0.1 gauss.

The circuit described by Thomas and Huntoon (16) was used as the basis for the construction of the bridge circuit to be employed in the present study. The two parallel tanks were constructed to resonate at the proper frequency. The

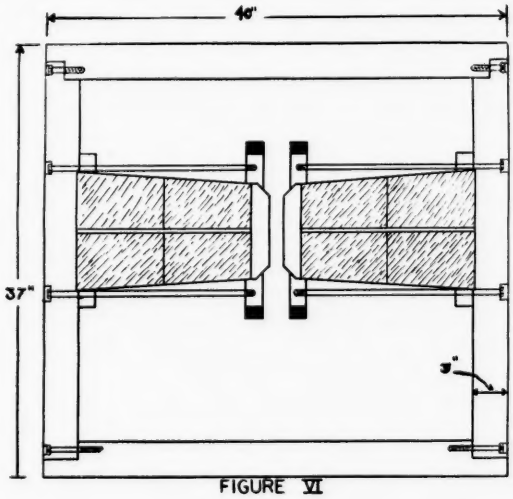


FIGURE VI

capacitors and the dummy tank were located inside a copper box with a lead going from the "high" side of the capacitor for the sample tank through the center of a $\frac{3}{4}$-inch brass tube to its associated inductance. This inductance was mounted so as to hold a test tube containing the sample vertically within the magnetic field. The brass tube was sufficiently long for the sample to be located at any place within the pole faces of the permanent magnet. The other component parts of the bridge were well away from the magnetic field and were electrostatically shielded by the copper box.

The resonance signal was observed by using a circuit identical to the one described by Thomas and Huntoon (16). The noise power was found to be of the same magnitude as the signal. This low value of the signal-to-noise ratio made analysis of the line shape impossible. The noise power was reduced by changing the crystal diodes as used in the original circuit to a double diode

vacuum tube. The coupling between the r-f signal generator was also changed from capacitive to inductive.

The advantages of the vacuum tube were its lower inherent noise and the fact that it separated the tanks by a high impedance. Inductive coupling made it

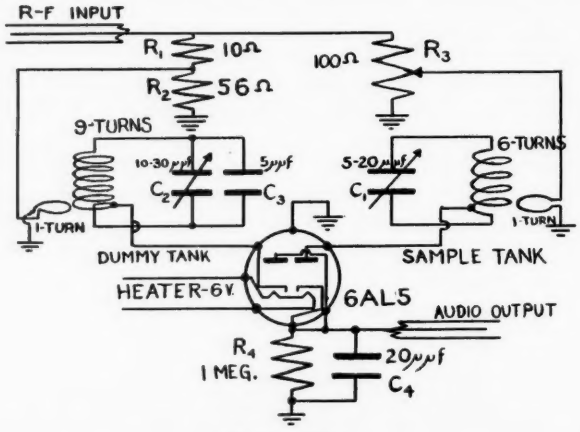


FIGURE VII-A

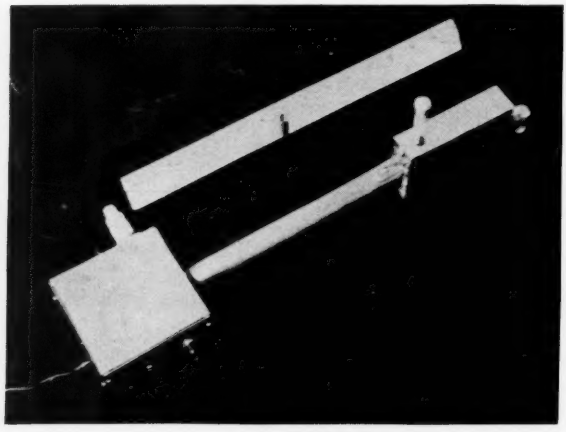


FIGURE VII-B

possible to introduce the required 180 degree phase difference between the two tanks by inverting one of the primary coils of the r-f tanks. This eliminated the easily detuned half-wave length cable employed in many circuits.

The resulting circuit is shown in Figure VII-A. It can be seen from the figure that the observed signal was coupled from the tank inductances at a point located ½ turn from the ground. This was done to avoid loading the tanks. The

two diodes had a 180° phase-relationship so that at amplitude and phase balance both diodes were either conducting or not conducting simultaneously. Under these conditions no signal appeared across R_4. The completed bridge circuit detector is shown in Figure VII-B.

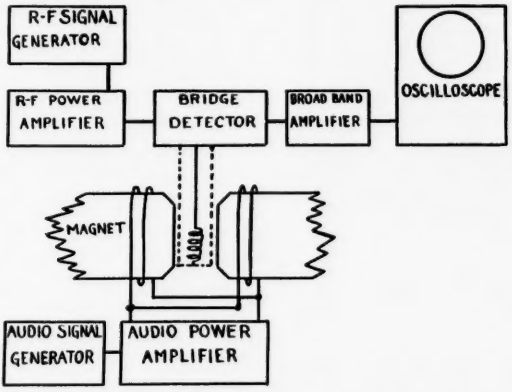


FIGURE VIII-A

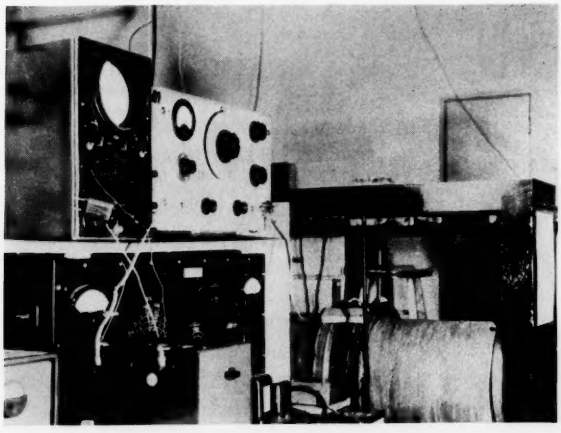


FIGURE VIII-B

The tanks were tuned to amplitude balance by adjusting potentiometer R_3 to give a maximum modulated r-f signal in the sample tank. With the dummy tank detuned and the sample in place, C_1 was tuned to give the maximum detected modulation signal across R_4. The sample tank was then shorted by adjusting R_3. Under these conditions C_2 was tuned for a maximum signal at the output. With both tanks tuned to the same frequency R_3 was adjusted until there was no output signal from the modulated r-f input signal appearing across R_4.

In operating under amplitude balance conditions the impedance of the sample tank was changed when the Larmor resonance conditions were satisfied. This change disturbed the balance between the two tanks resulting in a signal across R_4. Under balanced phase conditions, obtained by detuning the dummy tank slightly, the signal in the sample tank underwent a slight phase shift when the resonance conditions were satisfied. The balance was again disturbed and a signal appeared across R_4. Since the Larmor conditions were periodically satisfied by the modulated magnetic field, the detected signal was periodic. This periodic signal could be observed on an oscilloscope.

Figure VIIIA is a block representation of the complete experimental circuit. The r-f signal generator was a General Radio Model 805-C signal generator. Its output power was increased by using an r-f power amplifier from which the signal was coupled to the tank circuits in the bridge. The audio-frequency signal from the output of the bridge was amplified by a battery operated broad band amplifier from which the signal was coupled to a Du Mont Model 208-B oscilloscope.

The permanent magnet was modulated with a Hewlett-Packard Model 205-A audio signal generator which was coupled to a power amplifier. The output from this amplifier was applied to the modulation coils, which were wired in parallel. A photograph of the complete experimental array is shown in Figure VIII-B.

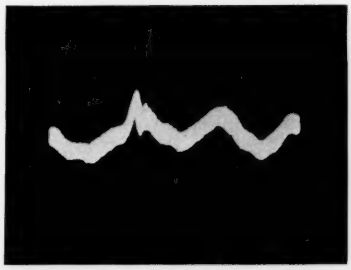
VI. EXPERIMENTAL RESULTS

Since the proton line in liquids is very narrow and appears as a very strong signal, it was not necessary to resort to the method of plotting output meter reading, as did Purcell *et al.* (11). In the present work, the nuclear magnetic resonance signal of the proton in water was studied as it appeared on the oscilloscope screen.

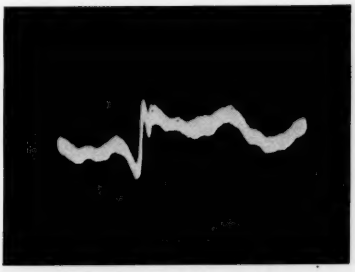
The reproductions which appear shortly are photographs of the patterns appearing on the screen of the oscilloscope which was fitted with a Du Mont oscilloscope camera. The magnetic field modulation amplitude was 2.6 gauss. This value was obtained by noting the voltage induced in a coil having a known number of turns and cross-sectional area at the desired output voltage of the audio-signal generator. The modulation frequency was 20-cycles/sec. which prevented the signal due to the large 60-cycles/sec. electromagnetic field in the room from traveling through the resonance signal as appeared on the oscilloscope screen.

If the frequency of the signal from the r-f signal generator is increased until the Larmor conditions are just fulfilled for the minimum value of the modulated magnetic field, the observed signal will appear like that shown in Figure IX-A. The process involved may be seen by referring to Figure II. This frequency is 33.2520 megacycles/sec. The other photographs in Figure IX were taken with successive r-f increments of about 4.0 kilocycles/sec. Photograph IX-G was taken at the "center frequency," obtained when the resonance phenomenon occurs at the field strength of the permanent magnet. The "center frequency" was assumed to be the frequency at which the resonance lines are equally spaced along the oscilloscope trace. The frequency so obtained may not be precisely the

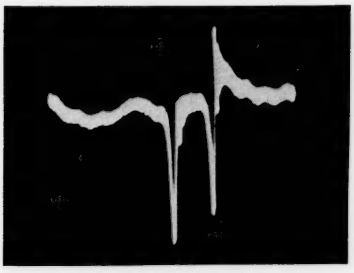
Larmor frequency for the field strength of the permanent magnet, since the oscilloscope sweep may not be linear.



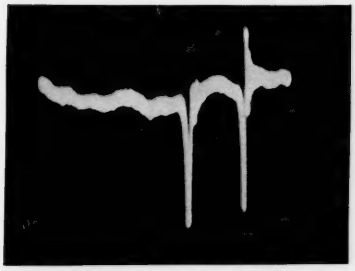
(A) = 33.2520 mc/sec.



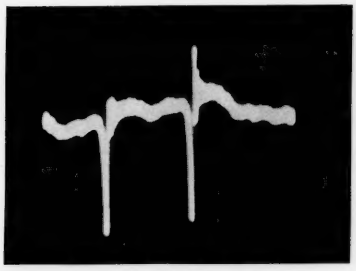
(B) = 33.2558 mc/sec.



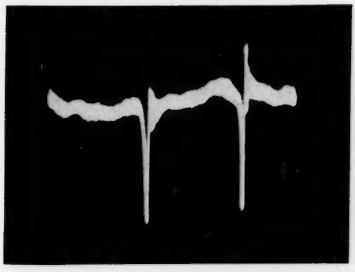
(C) = 33.2596 mc/sec.



(D) = 33.2634 mc/sec.



(E) = 33.2673 mc/sec.

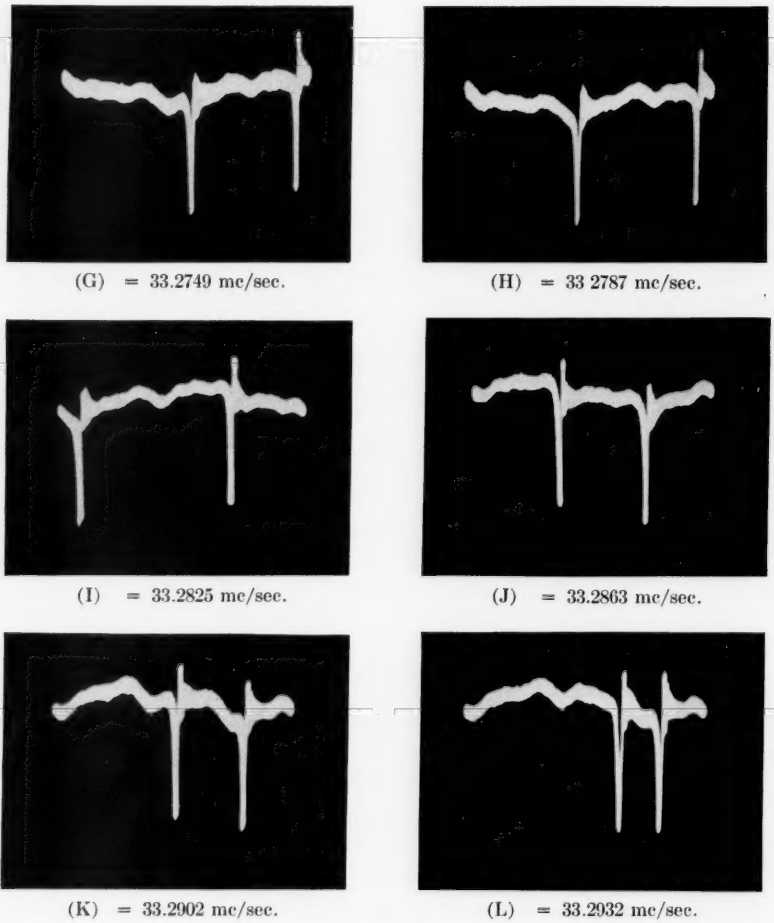


(F) = 33.2715 mc/sec.

FIGURE IX

This "center frequency" was checked by reducing the amplitude of the modulating signal. As this signal was decreased, the resonance line broadened, as expected. The frequency of the r-f signal had to be readjusted as the modulation was decreased so as to satisfy the Larmor condition for the new modulated field strength and keep the resonance signal on the oscilloscope trace. There is a minimum amplitude of the modulation signal required to modulate the external field sufficiently to pass through at least a fraction of the resonance line. As the modu-

lation amplitude decreases, the Larmor frequency approaches the "center frequency," which is the Larmor frequency for the steady field of the permanent magnet. The frequency given by this method was 33.2750 megacycles/sec.



(G) = 33.2749 mc/sec. (H) = 33 2787 mc/sec.

(I) = 33.2825 mc/sec. (J) = 33.2863 mc/sec.

(K) = 33.2902 mc/sec. (L) = 33.2932 mc/sec.

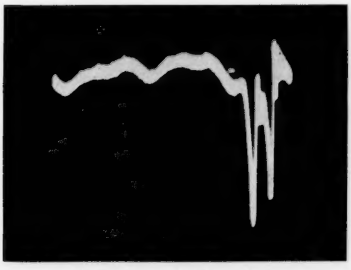
FIGURE IX

After passing through the center frequency, the series of photographs is continued at about 4.0 kilocycles/sec. intervals until the radio-frequency was too high for resonance to be observed. Figure IX-N shows the resonance line at 33.3016 megacycles/sec., the highest frequency for which the Larmor conditions can be satisfied for the given modulation field strength.

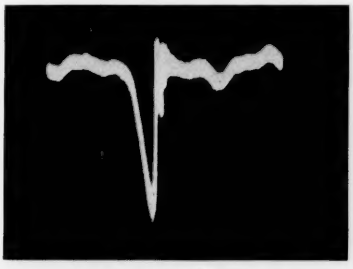
The width of the resonance line observed with the previously described apparatus was .055 gauss. This width was calculated by using the method as shown

in Appendix II. The shape of the line in these reproductions corresponds to pure absorption. It was also possible to achieve a good representation of the dispersive effects of the nuclear magnetic resonance line by detuning the dummy tank slightly. These dispersion lines, however, were not pure. There was always a slight asymmetry due to resonance absorption.

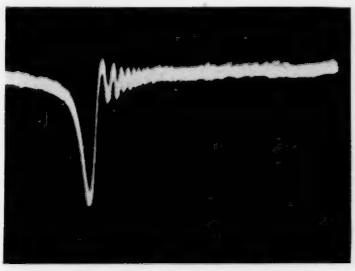
Figure IX-O is a reproduction of the line appearing at the "center frequency". The horizontal gain of the oscilloscope was increased so as to separate the "wiggles". Jacobsohn and Wangsness (19) gives a thorough theoretical description of these "wiggles". The classical explanation of these "wiggles" is that the nuclear spins, which have been tipped over by the application of the r-f field at



(M) = 33.2947 mc/sec.



(N) = 33.3016 mc/sec.



(O) = 33.2730 mc/sec.

FIGURE IX

their precessional frequency, will remain in this non-equilibrium position for a short period of time. These moments precess about the strong field at the instantaneous Larmor frequency independently of the rotating field and with a damping governed by the spin-spin relaxation time T_2. This varying signal from the nuclear precession thus comes alternately in and out of phase with the constant applied radio-frequency signal. The resulting "beats" appear on the oscilloscope screen as damped oscillations or "wiggles".

VII. MODIFICATIONS FOR BETTER RESULTS

The noise voltage introduced by the detection circuit can be greatly reduced by good construction techniques. There are, however, limitations in the reduc-

tion of the noise voltages which are presented by the well-known thermal agitation or Johnson noise, the shot effect, and the fluctuation voltages produced in vacuum tubes. Since these noises cover the whole frequency spectrum, there is no possibility of eliminating noise altogether. The noise power due to the Johnson effect is approximately 10 times that due to the shot effect and is much greater than that due to the fluctuation, or flicker, effect.

The power P associated with this Johnson noise has been shown to be $P = 2kT\Delta F$, (20, 21) where k is the Boltzmann constant, T the absolute temperature, and ΔF the band pass, or frequency range, of the amplifier. From this equation, it can be seen that by decreasing the band pass ΔF, the noise power is proportionally reduced.

The observed resonance signal is not a pure sine wave, but is composed of a fundamental and a large number of harmonics. Fourier's theorem shows that this wave shape may be represented as a sum of sine waves, or the function of the observed signal may be represented by:

$$\theta(t) = A_0/2 + \sum_{k=1}^{\infty} A_k \cos kx + B_k \sin kx.$$

The fundamental is given by the first term. This fundamental plus approximately 10 harmonics has been shown to give a very good representation of the actual non-sinusoidal wave shape of the type involved in this work. If, then, the fundamental and approximately 10 harmonics are present at the oscilloscope amplifier, the observed pattern on the screen should be a very good representation of the resonance line. In the problem presented here, the fundamental frequency of the observed pattern was 20 cycles/sec. This frequency plus its first ten harmonics, or all frequencies up to about 200 cycles/sec., should give a very good representation of the proton signal. The amplifier used in conjunction with this experiment has a band pass of from 175 to 2800 cycles/sec. From the Fourier theory, the band pass need only be 200 cycles/sec. Thus, a large part of the Johnson noise can be eliminated by decreasing ΔF to 200 cycles/sec. with no serious effect on the reproduction of the resonance line shape. The band pass can be reduced further by using a much slower sweep and, hence, having a smaller fundamental frequency. The reduction of this fundamental frequency is limited at very low frequencies by the amount of fluctuation noise which can be tolerated. This fluctuation noise is caused by uneven emission over the surface of the cathodes of vacuum tubes. The first stage will contribute the largest fluctuation noise because of the amplification following this stage. Experiments (22) have been conducted to determine the frequency of this noise. Below about 0.1 cycles/sec. the amplitude of the fluctuation noise increases down to 0.014 cycles/sec., which was the lowest frequency from which data were taken. A modulation frequency of approximately 0.1 cycles/sec. would thus be the optimum frequency for the modulation field. The random noise power would in turn be greatly reduced since the required band pass for a good reproduction of the nuclear magnetic resonance line is reduced to 1.0 cycles/sec.

Acknowledgements

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Appendix I

The Potential Energy of the Precessing Nuclear Magnetic Moment

The torque producing the precession of the nuclear magnetic moment about the field direction H_0 is given by:

$$L = \mu_I \times H_0 .$$

The magnitude of this torque is thus:

$$L = \mu_I H_0 \sin \theta,$$

where θ is the angle between the nuclear moment and the external field direction H_0. The potential energy is then given as:

$$U = \int L d\theta = \int \mu_I H_0 \sin \theta d\theta = -\mu_I H_0 \cos \theta + C.$$

The potential energy of a magnetic moment μ_I in an external magnetic field H_0, apart from an additive constant C, is thus:

$$U = -\mu_I H_0 \cos \theta = -\mu_I \cdot H_0 .$$

Appendix II

Calculation of the Line Width

The curve at the top of Figures X *A* and *B* represents the observed signal. The only possible ways for such a curve to be formed by the sinusoidal modulation field is shown by *A* and *B*. The reference time t_0 is arbitrarily taken to be halfway between two adjacent resonance signals. The magnitude of the field at any time is given by:

$$H = H_0 + H_1 \cos \omega t,$$

where H_0 is the permanent magnet's field strength, and H_1 the modulation field strength having a frequency ω. The time is given by $t = x/c$ where x is the displacement of the point in question on the oscilloscope trace from t_0 and c the velocity of the trace across the screen. Then:

$$H = H_0 \pm H_1 \cos (\omega x/c)$$
$$dH = \pm(\omega/c) H_1 \sin (\omega x/c)\, dx$$

or

$$\Delta H = \pm(\omega/c) H_1 \sin (\omega x/c)\, \Delta x$$

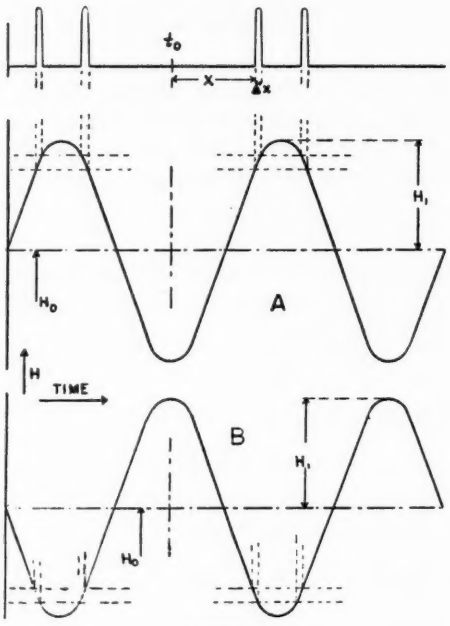

FIGURE X

but $\omega = 2\pi f$, and $c = D/T$, where D is the length of a complete trace and T is the period or time required for a complete trace to cross the oscilloscope screen and is given as the reciprocal of the frequency. Then $c = Df$, and

$$\begin{aligned}\Delta H &= (2\pi f H_1/(Df) \sin [(2\pi f x/Df)]\Delta x \\ &= (2\pi H_1)/D \sin [(2\pi x)/D)]\Delta x.\end{aligned}$$

APPENDIX III

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